Towards Quaternary Alloy Au-Pd Catalysts For Direct Synthesis of Hydrogen Peroxide

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Abstract

The direct synthesis of hydrogen peroxide (H$_2$O$_2$) in situ to replace legacy large-scale commercial anthraquinone synthesis is a critical industrial technology required to advance applications in sustainable green chemistry and reduce energy consumption associated with transporting reagents and oxidants. Current state-of-the-art Au-Pd transition metal alloy catalysts show promise to selectively synthesize H$_2$O$_2$ however activity is not optimal and material costs and sustainability concerns hinder widespread use. In this manuscript, using values from previously derived Oxygen Reduction Reaction (ORR) Volcano Plots, we analyze and filter potential AuPdMN {M=metal 1, N=metal 2} quaternary alloys by their associated descriptor values, the adsorption energy of mono-atomic oxygen and hydrogen. We report possible surface structures which have adsorption sites that optimize the adsorption energy of both descriptors and explain possibilities for using these results to leverage in future and ongoing work for truly optimal catalyst design for transition-metal alloys for direct synthesis of hydrogen peroxide. These results and recommendations should ultimately help increase the performance (activity and selectivity) of direct synthesis catalysts for hydrogen peroxide synthesis while simultaneously lowering the costs of materials in these catalysts and making them more sustainable.

Keywords: Oxygen Reduction Reaction, DFT, Catalysis, Hydrogen Peroxide, Alloy Catalysts, Green Oxidants

1. Introduction

Hydrogen peroxide (H$_2$O$_2$) is one of the most common household chemicals and it also has many uses in industrial processes. Such uses include as pharmaceutical disinfectant, an effective oxidant and a growing use in the pulp and paper industry, and can be an {undesired} product of the 2-electron transfer in the Oxygen Reduction Reaction (ORR) relevant to Proton Exhance Membrane Fuel Cells (PEMFC). [1–5] The main benefit of using H$_2$O$_2$ in such roles is that it can be a “greener” alternative to many of the other oxidants in use today. Accordingly, it is being looked at as a replacement for many of the common household cleaners and ingredients for laundry detergent. [3, 5] Hydrogen peroxide is also used in municipal wastewater treatment for the removal of contaminants such as hydrogen sulfide, cyanide, nitrite and many more. [5]

Hydrogen peroxide is primarily produced through the anthraquinone auto-oxidation process. [6, 7] This process is an indirect synthesis that uses organic solvents to achieve the formation of H$_2$O$_2$ which avoids the use of H$_2$/$O_2$ mixtures. The avoidance of using such a volatile mixture is one of the primary advantages that the anthraquinone process provides. However, due to high capital and operating costs, this process is...
only economical when performed on a large scale which prevents many companies that need the chemical for their processes from producing it on a small scale in situ. This scenario also creates a need for H\textsubscript{2}O\textsubscript{2} to be transported which introduces even more cost and safety concerns since H\textsubscript{2}O\textsubscript{2} can decompose explosively. [5, 6] Beyond the cost and safety concerns previously mentioned, degradation of the ethylanthraquinone, one of the reactants along the pathway to form hydrogen peroxide, is a major concern for the efficiency of this process. Ethylanthraquinone degradation is also correlated with the deactivation of the palladium catalysts used in the process which also decreases the efficiency and increases the cost of the process. [8, 9]

One of the methods currently being investigated to minimize the issues that are associated with the indirect synthesis of hydrogen peroxide is using direct synthesis. If H\textsubscript{2} and O\textsubscript{2} can be safely extracted from common sources such as air and water, then given the right catalyst(s), H\textsubscript{2}O\textsubscript{2} can be produced on a smaller scale in situ which will also help eliminate transportation concerns, contributing to its value as a "greener" oxidant. Therefore, in hopes of reducing the cost and eliminating some of the safety concerns of hydrogen peroxide production, researchers are looking at determining a catalyst for the direct synthesis of hydrogen peroxide (DHPSP). Currently, AuPd catalysts have been shown to be the current state-of-the-art catalysts in regards to activity and selectivity for this reaction. In this context, the use of selectivity to mean the ratio of desired to undesired products and , correspondingly, activity meaning the multiplicative factor increase in the rate of the reaction as compared to the uncatalyzed reaction. However, because Au and Pd are both rare metals, the primary concerns are the cost and sustainability of such catalysts. Another concern is that while Au-Pd based alloy catalysts currently show state-of-the-art performance for the DHPSP, the selectivity and activity can be improved according to the predictive Volcano Plot(s) previously generated for the ORR on single crystal transition metal catalysts. [1]

Xu et al. reported that Pt as an alloying metal to AuPd catalysts provides better activity while retaining great selectivity. [10] They also predicted that W, Pb, Mo, and Ru would also be good candidates to form ternary catalysts with Au and Pd. Mahata and Pathak looked at binary and ternary compounds composed of Co, Au, and Pt. [11] They concluded based on energy barriers for the desired and undesired reactions of the direct H\textsubscript{2}O\textsubscript{2} synthesis pathway (DHPSP) that Au\textsubscript{10}Co\textsubscript{9}Pt\textsubscript{60} was highly selective towards H\textsubscript{2}O\textsubscript{2} production and therefore the best of the alloys tested. Nugraha et al. studied Pd-Au and Pd-Hg catalysts in comparison to pure Pd. [12] Their results concluded that Pd-Hg and Pd-Au showed similar properties and are both better than pure Pd. Other works have examined the structure of the Au-Pd catalyst and determined possible methods of improving the selectivity and activity of the catalyst. These works studied varying lattice strain, changing the arrangement of the atoms, and different layering in the sub-surface structure. [13–15]

The new results in this manuscript are based on density functional theory (DFT) calculations. The focus was on two different aspects of interest to help understand how to improve the Au-Pd catalyst system. First, eight different AuPd surfaces with different arrangements of the Pd and Au atoms were studied. This was done with the purpose of determining whether the arrangement of the atoms significantly changes the \( \text{O}^* \) and \( \text{H}^* \) binding energies which are descriptors for the activity and selectivity of AuPd catalyst. [1] (Descriptors are key variables or parameters upon which all other properties of the system can be correlated to and predicted from.) In addition to these tests, the AuPd surfaces were alloyed with other transition metals (Pt, Rh, Ir, Ag, Cu, and Ni) to determine if these alloying metals could simultaneously increase the activity and selectivity of the catalysts and decrease the rare metal content of the catalysts. This alloying was done through random substitution of two atoms of Au to either Ag, Cu, or Ni and two atoms of Pd to either Pt, Rh, or Ir, which are closer to Pd in electronic structure, to form quaternary alloys of (AuPd)\textsubscript{88}(MN)\textsubscript{12} composition. (See details in November 7, 2019
Among the 576 different systems (combinations of surface, site, and composition) reported in this manuscript, 72 fell within the desired range for the ideal catalytic activity and selectivity. Over a third of these variations were pure Au-Pd systems which indicates that Au-Pd catalyst with varying surface structure and local adsorption-site compositions are innately well-suited as among the best catalysts for the direct synthesis of H$_2$O$_2$, but they can still be improved in activity, selectivity, and most significantly cost. The remaining systems varied throughout the range of combinations studied in this work. However, systems with Pt and Ag and systems with Rh and Ag had the most frequent occurrences. While the introduction of Pt has shown promise in increasing catalytic activity for the DHPSP in other work, it does not solve the cost issue associated with rare metals. [10] The same can be said for Rh unfortunately. However, the introduction of Ag would help with cost reduction and future research may be warrant to study the effect of Ag more. The use of Ir, Ni, and Cu also showed promising results, but these were not as numerous frequent) as the results seen for Pt, Ag, and Rh. 

This work reported in this manuscript is not intended to be an end-all investigation complete predictive design of the best Au-Pd based DH-PSP catalyst. Instead, this work is designed to pre-filter materials and guide future studies which leverage the results presented in this work to move closer to optimal DH-PSP catalyst design. The results presented in this work prove the first step in helping move such progress forward by proving that at least some of the quaternary AuPd$_{88}$(MN)$_{12}$ catalysts have at least a fraction of their surface sites which have descriptor values for activity and selectivity that fall very close the to predictive Volcano Plot peak. Further investigation is warranted though, especially for Ni and Cu systems, because like Ag they would help decrease the cost of the catalyst. Ongoing and future work related to this project is underway and will focus on studying the to-date best identified composition(s), surface structure, adsorption sites (by way of descriptor values) as a function of varying composition (decrease AuPd loading) and varying catalyst surface order/disorder (random alloy, intermetallic, core-shell, etc).

2. Methods

2.1. DFT Calculations

Plane-wave DFT calculations were performed to study the energetics of both the mono-atomic oxygen and mono-atomic hydrogen adsorbate atoms on the catalyst surface(s). These adsorption energies serve as explicit descriptors of activity and selectivity, on the Au-Pd based surfaces described in this work. [1] Plane-wave DFT calculations accurately reproduce both the quantitative and qualitative trends in the activity and selectivity for single crystal surfaces of transition metal catalysts for the ORR. [1, 2, 16–20] The settings and parameters for these calculations are described below.

The calculations were performed using the Medea v2.21 Vienna Ab Initio Simulation Package (VASP) from the Materials Design Company. [21–25] The GGA-rPBE functional was chosen for these calculations which is able to qualitatively and quantitatively reproduce the experimentally observed ORR activity and selectivity trends for the type of materials described in this work. [16, 18–20, 26–30]

Spin polarization was allowed for some of the RhNiAuPd and IrNiAuPd systems because otherwise the calculations would not converge since Ni is inherently ferromagnetic. The cutoff energy for the plane-waves for all calculations was 400 eV. The electronic wavefunctions were relaxed until a convergence of at least 10$^{-6}$ eV was reached. The Methfessel-Paxton 2$^{nd}$ order algorithm was used to treat the smearing of the electronic wavefunctions near the Fermi Energy with a value of 0.2 eV. [31] The initial relaxation of the atomic positions (to net magnitudes < 0.05 eV/Å) was performed through k-point sampling on a 1x1x1 γ-centered grid, then refined on a 2x2x1 γ-centered grid. For this refinement, the top two slab layers’ and the adsorbate atoms’ geometries were relaxed to net force magnitudes of less than 0.02 eV/Å in
all directions of the calculation cell. Spurious interactions between slabs were reduced by applying dipole corrections parallel to the surface normal.

Calculations were performed for eight different Au-Pd surfaces with mono-atomic Hydrogen(H*) and mono-atomic Oxygen(O*) used as adsorbates at nine different high-symmetry 3-fold FCC positions, given the calculation cell size corresponding to a nominal coverage of 1/9 ML. Initial calculations were performed to determine the two best FCC positions for each surface. (Best as determined by most exothermic adsorption energy FCC sites) These eight surfaces were then alloyed with other transition metals using the random substitutions function within MedeA. Pd was substituted using Pt, Rh, and Ir while Au was substituted with Ag, Cu, and Ni. Four randomly alloyed surfaces per quaternary composition were generated for each of the initial Au-Pd surface-position permutation calculations. These calculations were run using the already relaxed surfaces generated from the initial calculations and freezing the atoms in these generated surfaces. From here, single point calculations were used after adsorbate structure optimization to accelerate the screening process.

2.2. Slab Procedure

To construct the calculation slab/cell models reported in this work, the following procedure(s) were employed. The lattice constants of 8 bulk Au-Pd 50:50 alloys of random compositions were optimized in VASP with 64 atom supercell beginning at a lattice constant of 4.07 Angstroms. The resulting optimized lattice constants were averaged and the corresponding value of 4.064 Angstroms was used moving forward in construction of the slab models. This lattice constant was used when creating 8 new randomly ordered Pd-Au bulk alloys of 64 atoms each. For each of these 8 bulk configurations, the built in surface generator of MedeA was used to orient the crystal along the {111} direction and truncate it to 4 slab layers thickness. The surface primitive cell was expanded such that a net p(3x3) surface cell of Au$_{18}$Pd$_{18}$(111) was created. This slab was then optimized under the same force criteria outlined above with the 2 top layers relaxed and the bottom 2 layers constrained in all directions. The geometric structure of these 8 random Au$_{18}$Pd$_{18}$(111) surfaces are shown in Figures SI.1-SI.8 of the Supporting Information. For each of these Au$_{18}$Pd$_{18}$(111) surfaces, there are 9 distinct 3-fold FCC sites which have varying local structure. The adsorption energy of the descriptor species, O*, and H* were studied on the lowest-energy sites identified for these Au$_{18}$Pd$_{18}$(111) surfaces, and the alloy surfaces created therefrom. These results are discussed in the section that follows.

3. Results and Discussion

3.1. Background and Correspondence to Previous Volcano Plot

As previously mentioned, Au-Pd catalysts are currently the best for the direct synthesis of H$_2$O$_2$. It was determined from the calculations for this work that structure is a very important factor in the determination of the effectiveness of a catalyst with respect to both activity and selectivity. Our calculations from MedeA-VASP output 'raw' energies in units of kJ/mol. These must be converted to units of eV and in the same reference basis as used in the work where the prior Volcano Plot was created and identified.$^1$ On a scale of $\Delta E$ for the adsorption of O where: $\Delta E_{ads} = (E_{sys} - E_{bare surface})/96.5 + 7.06$, around 2.0 eV is the ideal binding energy to maximize activity while remaining in the H$_2$O$_2$ selective region.$^1$ The calculations in this work yielded values for $\Delta E_{ads}$ on Au-Pd catalysts ranging from 1.35 to 2.99 eV. A few systems had $\Delta E_{ads}$ above 3 eV, but these were excluded from this part of the analysis because they would be far too weakly binding if they even bound at all. These values had an average of 2.24 eV and a standard deviation of 0.37 eV. It was determined that a range of 1.9-2.1 eV would capture the systems close enough to the ideal 2.0 eV to warrant further analysis. The average for Au-Pd surfaces falls outside of that range and the standard deviation is large. Since all of the Au-Pd
surfaces tested had the same overall stoichiometric composition, the deviation in binding energy had to do with the atomic structure of the binding sites, more specifically the composition of the atoms immediately surrounding the site. The systems identified in this work to have the optimal combination of descriptor values are shown beginning in Figures 1 and 2. The non-uniformity of the systems on a surface by surface basis is apparent in Figures 3-10.

It was the larger goal of this study to use alloying metals to possibly discover a surface with more consistently 'optimal' \( \Delta E_{\text{ads}} \) energies while maintaining or possibly even improving activity and selectivity for direct \( \text{H}_2\text{O}_2 \) synthesis. These improvements were measured by using the adsorption energies for \( O^* \) and \( H^* \) as descriptors for activity and selectivity. The desired filtering level values for these descriptors were between 1.9 and 2.1 eV for \( O^* \) and between -0.15 and 0.15 for \( H^* \). In addition, alloying with less rare metals than Au and Pd would hopefully provide a decrease in cost for such surfaces.

For the systems tested two atoms of Pd were substituted with Pt, Rh, or Ir and two atoms of Au were substituted with Ag, Cu, or Ni to create a total of nine different substitution combinations. These substitutions were done randomly in four iterations. The best two sites from the AuPd calculations were selected for these substitutions. With eight different surface structures the total number of systems tested was 576. In addition to O adsorption energy, the systems were filtered based on H adsorption energy, this will be discussed more in a later section. Out of the 576, 72 of them fell within both of the filter ranges.
These systems represented those with the desired activity and selectivity for direct hydrogen peroxide synthesis. We also note the very interesting results shown in Figure 1 (and 2) decomposed on a surface-by-surface basis in Figure 3 through Figure 10 show very different slope and intercept(s) when correlating the adsorption energy of hydrogen to oxygen on a given catalyst surface and site. This deviation from perfect linear scaling is an ongoing pursuit in current computational catalyst design for the oxygen reduction reaction (ORR) in seeking non-Platinum catalysts. At least for adsorption of O and H on Au-Pd based catalyst surfaces, the local adsorption site structure and doping via quaternary alloying elements seems to easily achieve this breaking of linear scaling.

3.1.2. Data In Total (Adsorption Heatmaps)

All of the data collected for this paper is displayed on nine different heatmaps assembled and shown as panels shown in Figure 11. Each heatmap corresponds to one of the nine adsorption sites previously discussed. The vertical axis for each heatmap gives the compositions of all of the systems tested. The horizontal axes indicate the surface structure of the systems based on the eight tested in this study. Two things of note
are that the first two heatmaps are only eight solid columns corresponding to only one composition and that on the remaining heatmaps there is a significant amount of void space. Both of these apparent abnormalities can be attributed to the aforementioned process that was used in only selecting the best two sites from the eight pre-substitution AuPd surfaces. This means that for the surfaces studied in this work sites 1 and 2 did not have the best bonding strength and the same could be said for the site and surface combinations that results in void space in the other seven heatmaps.

The color on the heatmaps indicates the strength of Oxygen binding to the surface. It ranges from dark blue to dark red with variations of blue, red, yellow, and green in between as shown by the color bar. The dark blues segments indicate systems that bind too strongly while the dark red segments indicate systems that bind too weakly. The systems that have the desired bond strength are shown to have a light green color on the heatmaps. Out of the green segments on
the heatmaps, the most common composition(s) included Au-Pd and quaternary variations that included Pt, Ag, and Rh. Ir and Ni generally yielded systems that were too strongly binding. Other patterns are apparent on a surface by surface basis. Surface 2 seemed to have Oxygen bind too strongly, even indicating a deviation in other patterns such as that described for Ir and Ni. Surfaces 1 and 7 showed evidence of being too weakly binding. This means that the structure of the surfaces had a significant impact on the binding energy of Oxygen and in some cases even more significant than the substitution of transition metals into the systems.

As mentioned before, the systems that fell into the desired range of Oxygen adsorption energies were filtered out and used for further analysis. Figures 12 and 13 both show these systems, but on different scales for the adsorption energies. Figure 14 further constrains the range for the adsorption energies while plotting by the best systems on a composition basis. As indicated by the heatmaps and these plots, the best systems had a combination of one strongly binding metal such as Ag and one weakly binding metal such as Pt or Rh. Therefore, for future work we recommend systems that include similar combinations that may include Ni or Fe with Ag.

3.1.3. Comparison to Experiment and Compositional Analysis

As previously mentioned, the common alloying elements of the systems that fell within the desired range of O adsorption energy were Rh, Pt, and Ag in addition to Au and Pd. While no absolute quantitative comparisons of descriptor values could be made, there are several patterns and qualitative properties that were comparable to previous works. The first of these comparisons relates to the work done by Xu et al. They determined that AuPdPt has a greater activity for the production of hydrogen peroxide than AuPd. [10] Since all of the substituted systems in this work are quaternary systems there is no direct comparison, but based on the volcano plot from the work by Rankin and Greeley a comparison was made based on O bonding strength. The volcano plot indicates that the theoretical addition of Pt to an Au-Pd system would bring the system closer to the volcano peak meaning the activity of the system would increase. [1] This also means that the binding energy would slightly decrease. The calculations for this work support this. In general, the systems containing Pt have slightly lower binding energies than the Au-Pd system for the same surface. Also, many of the systems do not deviate from the desired range by much, therefore the systems maintain a decent selectivity further supporting the work by Xu et al.

Nugraha et al provided the adsorption energies for Pd(111), Pd₆Au₃(111), Pd₆Hg₃(111), Pd₆Au₃(111), and Pd₆Hg₃(111). [12] The values for these adsorption energies used a different reference state basis than those used for this work, however when they are adjusted by a factor of 3.07 eV to match the scale for ∆G for this paper, the Pd₆Au₃(111) system falls right near the target line. This is shown in Figure 13. Given that Nugraha and company claimed that Pd₆Au₃(111) and Pd₆Hg₃(111) were the best of the systems they tested, there is a good amount of confidence in the systems are near the target line of 2.1 eV. However, it is worth noting that these systems are richer in Pd and therefore would be expected to bind to O* and H* more strongly, therefore the straight addition to adjust the scale may not be
absolutely quantitatively accurate. Qualitatively though, the systems Nugraha and company tested that are closest to the ones studied in this work do appear to fall in the general range of adsorption energies as would be expected.

Figure 13: Data is shown for the comparison between the best candidates, the pure catalyst, and some values from literature. [10–12] Work in this manuscript is shown in orange circles. The target adsorption energy for O* is shown on the vertical orange line. Values from single crystal pure-element studies are shown at the bottom of the plot. [1]

The previously talked about volcano plot by Rankin and Greeley was the basis for the filtering of the raw data to get the most promising candidates. [1] In that work a selectivity region where the descriptors favor selectivity for the formation of H$_2$O$_2$ is overlaid on the activity Volcano Plot. The red triangle is the volcano peak where the activity of the reaction is the highest. The region in the black selective region closest to the red high-activity Volcano Peak is therefore the optimal active and selective H$_2$O$_2$ synthesis catalyst. Therefore, the ideal catalyst would fall around 2.1 eV for the O adsorption energy and about -0.2 eV for the H adsorption energy using $\Delta G_{\text{ads}}$ as the descriptor corresponding to that used in the earlier work. For this work a range of 1.85 to 2.25 eV was used to filter the systems by O adsorption energy and a range of -0.035 to -0.335 eV was used to filter them by H adsorption energy. Going back to Figures 1, 12, and 14, while Ag, Rh, and Pt had the most potential candidates based on the filtered data, it is worth noting that systems containing Ir and Ni fell close to the ideal H adsorption energy. This means that these elements as alloying components may still have potential for improving catalysts.

As mentioned above, Figure 13 shows the adjusted values from the work of Nugraha et al. However, it also shows the 72 data points selected from this work as the best among 576 systems and the four pure metal points from Rankin and Greeley’s work. Also, on the plot are the qualitative listings from Xu et al along with Mahata and Pathak. These two listings give the systems studied in their respective works in order of activity.

3.1.4. Implications for Optimal Hydrogen Peroxide Synthesis Catalysts

Possible avenues for future research were discussed earlier, but rather briefly, a more in-depth discussion is provided in this section. Figures 15 and 16 provide a look at the 72 filtered systems from this work compared to the ideal mixing values for the same systems based on the volcano plot by Rankin and Greeley (using a stoichiometrically weighted average of the descriptor values for the single-crystal metal surfaces). The predicted descriptor values using ideal mixing were calculated using the chemical formulas from the DFT calcu-
lations. The predicted adsorption energies were calculated using the percentage of atoms of each element were in a system multiplied by the pure metal value from the volcano plot. The sum of these values for a system was the ideal descriptor value. **Figure 15** shows this comparison for the O adsorption energies. The R$^2$ value for the fit of this plot was 0.0685 and the MSE was 0.0095 for an average real adsorption energy of 2.11 eV. **Figure 16** shows the same comparison for the H adsorption energies. The R$^2$ value for the fit of this plot was 0.218 with an MSE of 0.0032 for an average of -0.175.

![Figure 15](image1.png)

**Figure 15**: Data is shown the comparison between the real (calculated) Oxygen adsorption energy and predicted ideal mixing adsorption energy for all of the best candidate surfaces.

Both of the R$^2$ values are very low which indicates a very weak correlation, in fact the O adsorption energies appear to have almost no correlation. Unfortunately, this means that using ideal mixing comparisons is not going to be a quantitatively valid screening process for future testing and DFT calculations will still have to be used to determine absolute descriptors for potential candidates for catalysts for the direct synthesis of H$_2$O$_2$. However, the MSE values are also very small which indicates a small average error in the scatter around the fit. This means that while DFT calculations would still be required to get accurate results, using the ideal mixing assumption as a first pass filter can at least narrow the field of possible candidates of systems that should be tested since the errors are systematic small across all compositions/structures. The strong deviation from ideal mixing indicated by the R$^2$ values does confirm the idea that the structure of the catalyst and the identity of the atoms surrounding the adsorption sites has a significant impact on the effectiveness of the catalyst; this effect dwarfs the overall bulk-property that can typically be assumed in alloy-based studies.

This deviation from ideal mixing also leads to the possibility that adding significantly more of an alloying metal such as Ni or Ag might be able to provide the desired activity and selectivity while reducing the rare metal content. Creating such a catalyst would significantly decrease the cost of the DHPSP making it a more viable option for hydrogen peroxide production.

Future and ongoing work will consider using combinations of alloying metals that use one too weakly binding metal and one too strongly binding such as Ni and Ag. Compositional loading effects will be examined with more heavily alloyed catalysts and to see at what point the alloying starts to overwhelm the functionality of the catalysts. Continuing to vary the alloying metals and their concentration(s) and surface structure/site-composition will hopefully provide...
further improvements to hydrogen peroxide production by creating catalyst surfaces which possess large number of "optimal" active sites.

4. Data Availability

The raw/processed data required to reproduce these findings is available by request to the corresponding authors. They cannot be shared in full to public at this time as they constitute part of an ongoing study.

Acknowledgments

R.B.R. gratefully acknowledges financial and research support from the Department of Chemical Engineering at Villanova University through his startup package fund. C.W. and S.A. acknowledge financial support from the Department of Chemical Engineering and the College of Engineering at Villanova University as well. All the authors acknowledge assistance from U.N.I.T. team at Villanova University for maintenance of computational resources necessary in this work. R.B.R., C.W., and S.A. declare no conflicts of interest, financial or otherwise.

References


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Figure SI.1: \( p(3\times3) \text{Au}_{50}\text{Pd}_{50}(111) \) calculation cell of Surface 1, with Site #1 shown via an adsorbate atom in white. Au (yellow), Pd (blue). View is straight down to surface; 3 atomic layers of slab can be seen via choice of CPK Scale.
Figure SI.2: \(p(3\times3)\) Au\(_{30}\)Pd\(_{50}\)(111) calculation cell of Surface 2, with Site #3 shown via an adsorbate atom in white. Au (yellow), Pd (blue). View is straight down to surface; 3 atomic layers of slab can be seen via choice of CPK Scale.
Figure SI.3: $p(3\times3)$ $\text{Au}_{50}\text{Pd}_{50}(111)$ calculation cell of Surface 3, with Site #4 shown via an adsorbate atom in white. Au (yellow), Pd (blue). View is straight down to surface; 3 atomic layers of slab can be seen via choice of CPK Scale.

Figure SI.4: $p(3\times3)$ $\text{Au}_{50}\text{Pd}_{50}(111)$ calculation cell of Surface 4, with Site #2 shown via an adsorbate atom in white. Au (yellow), Pd (blue). View is straight down to surface; 3 atomic layers of slab can be seen via choice of CPK Scale.
Figure SI.5: \( p(3\times3) \) Au\(_{50}\)Pd\(_{50}\)(111) calculation cell of Surface 5, with Site #6 shown via an adsorbate atom in white. Au (yellow), Pd (blue). View is straight down to surface; 3 atomic layers of slab can be seen via choice of CPK Scale.
**Figure SI.6:** p(3x3) Au$_{50}$Pd$_{50}$(111) calculation cell of Surface 1, with Site #9 shown via an adsorbate atom in white. Au (yellow), Pd (blue). View is straight down to surface; 3 atomic layers of slab can be seen via choice of CPK Scale.

**Figure SI.7:** p(3x3) Au$_{50}$Pd$_{50}$(111) calculation cell of Surface 7, with Site #7 shown via an adsorbate atom in white. Au (yellow), Pd (blue). View is straight down to surface; 3 atomic layers of slab can be seen via choice of CPK Scale.
Figure SI.8: p(3x3) Au$_{50}$Pd$_{50}$(111) calculation cell of Surface 8, with Site #5 shown via an adsorbate atom in white. Au (yellow), Pd (blue). View is straight down to surface; 3 atomic layers of slab can be seen via choice of CPK Scale.