

Novel Surface Architecture Synthesis for Gas Separation and Fuel-Cell Catalyst Applications

James Guthrie, Georgia Institute of Technology, SURF 2010 Fellow

Advisor: Dr. Faisal Alamgir; Mentor: Robert Rettew

Introduction

One of the limiting factors in the economic feasibility of fuel cells is the great cost of catalyst materials necessary for reactions with the cell. One solution for this issue is the use of a bimetallic, whereby a core of one material is coated by an atomically thick shell of a more catalytically active material. One such set of materials is a Pt shell on a Au core. The process by which we attain an atomically thick Pt coverage of a Au substrate is surface limited redox replacement (SLRR). This technique is one in which a less noble metal is deposited in one atomic monolayer (ML) via underpotential deposition (UPD) and then electrolessly replaced by the desired more noble metal. This process has been used for a variety of applications and shows promise because of the resulting bi-metallic effect in which the catalytic activity of the combined core-shell metals is greater than either metal individually. The cause of this phenomenon is unknown, and is one of the facets we're investigating. In the process of trying to discover the cause of the bimetallic effect, we discovered another interesting phenomenon: when a bi-metallic structure is cycled as the catalyst of methanol redox, the Pt layer is removed, but in what seems to be a two-part process. Thus the main focus of our research this summer became the determination of the processes by which Pt was removed from the Au surface. To this end, the hope was to treat a Pt/Au bimetallic structure with iodine, and then determine coverage changes as a function of methanol cycling by looking at the different surface Woods structures created by the adsorption of iodine. To look at the surface structures, which are different for Au and Pt, a scanning tunneling microscope (STM) was used. The doping is necessary because of the difficulty of atomic resolution on an STM, especially of Au. The problem being that Au atoms are notorious for "clinging" to an STM tip and thus ruining the atomic sharpness of the tip.

Procedure

For the purpose of discovering the process of Pt removal, instead of using a core-shell nanoparticle, Pt was deposited onto a flat surface substrate. Three separate substrates were used, Au(111), a Au coated slide, and template stripped Au on a glass slide. The Au(111) samples were polished to 0.5 μm using a Masterprep suspension. All electrochemistry was done on a Pine Wavenow potentiostat and with a homemade Ag/AgCl reference electrode. The Pt deposition structures were formed on the Au by UPD of Cu on the Au substrate from a solution of 10mM CuSO_4 + 50mM H_2SO_4 , which had been deaerated with dry nitrogen for 10 minutes before deposition, followed by 10 minute immersion in 1mM H_2PtCl_6 in DI water to replace the ML of Cu with 0.3ML of Pt. During UPD of Cu on Au, there are two steps of UPD, one which deposits $\sim 0.6\text{ML}$ of Cu, and the second which deposits the remaining part of the full ML [1]. For our fabrication we held at a voltage between these two steps, and thus deposited $\sim 0.6\text{ML}$ of Cu. During immersion in the Pt solution, the replacement takes place in a 2:1 Cu:Pt ration, thus resulting in our figured $\sim 0.3\text{ML}$ of Pt placed on the sample per iteration. To get to full ML coverage, we simply iterated these steps.

For KI adsorption, cyclic voltammetry was done in 1mM KI to determine the voltage domains for the two different well documented Au woods formations [2]. The same was not necessary for the Pt formation, as it does not significantly change over different voltages [3].

STM work was done using electrochemically etched tungsten tips on a Nanoscope II STM, which is the property of the Bottomley research group, inside a vibration isolation chamber.

Results and Discussion

The electrochemistry done initially of the Pt/Au substrate as the catalyst for methanol redox, and subsequent XPS (Figure 1), is what initially lead us to interest in the Pt morphology changes during the

redox process, and thus design of the iodine doping and STM experiments.

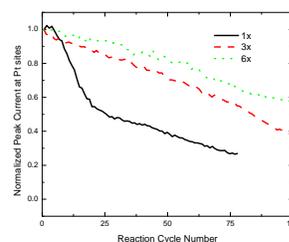


Figure 1: XPS of Au/Pt samples showing the decrease in Pt signal as a function of cycle number in methanol

For the determination of the voltage ranges for the two woods structures, one of which we thought would be sufficiently different than the Pt structure, a cyclic voltammogram of Au in 1mM KI was done (figure 2).

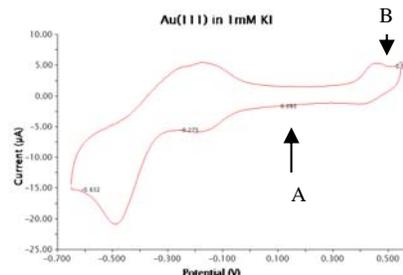


Figure 2: CV of Au in 1mM KI, with A) centered rectangular and B) rotate hexagonal reconstructions.

Unfortunately, however, atomic resolution was never realized using the STM. The STM did show us that the Au(111) substrates weren't flat and terrace free enough to be used with STM for the analysis we desired, hence the shift from Au(111) to Au covered slides and finally to template stripped Au.

Conclusion

The conclusions we had hoped to come to by the end of the summer obviously weren't realized, and doubt has been thrown upon whether our experimental was feasible or not. Due to this setback, however, I will be continuing to work on this project for the next couple weeks after the program and before the start of the Fall semester. The plan is to try a few more times for the atomic resolution, and then to potentially try low angle XRD to find the conclusions we seek.

References

- [1] Hachiya, T. and Honbo, H. et al. Detailed Underpotential Deposition of Copper on Gold(111) in Aqueous-Solutions. *Journal of Electroanalytical Chemistry* **1991**, 315, 275-291.
- [2] Yamada, T., Batina, N., Itaya, K. (1995). "Interfacial structure of iodine electrodeposited on Au(111): studies by LEED and in situ STM." *Surface Science* **335**: 204-209.
- [3] Schardt, B. C., S. L. Yau, et al. (1989). "ATOMIC RESOLUTION IMAGING OF ADSORBATES ON METAL-SURFACES IN AIR - IODINE ADSORPTION ON PT(111)." *Science* **243(4894)**: 1050-1053.