eNMR for In-Situ Fuel Cell Catalyst Characterization

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Objectives

The broad objectives of this research are to develop and apply high resolution electrochemical NMR to the characterization of fuel cell catalysts under *in situ* conditions. Specifically, we will use various solid-state NMR (ssNMR) methods to achieve the high resolution characterization of adsorbates at the active, catalytic surface of a functioning fuel cell electrocatalyst based on Au nanoparticles (NPs).

Technical Barriers

At present, one of the constraints to wide application of fuel cell technology is poor performance of the dioxygen cathode electrocatalyst. Also, there is substantial interest in the application of non-Pt based electrocatalysts. This effort seeks to develop eNMR as a technique that can be used to characterize and understand the chemisorbed state of adsorbates at nanoparticle-based fuel cell cathode electrocatalysts. Based on intriguing reports of unusual catalytic activity for Au NPs and certain crystal faces of Au,[1,2] we are developing and implementing eNMR as a method for characterizing such electrocatalysts.

Abstract, Progress Report and Future Directions

Abstract

We describe the synthesis of $Au_{101}(PPh_3)_{21}Cl_5$ (Au_{101}) and citrate-capped Au nanoparticles (NPs) using wet techniques. These Au NPs have been characterized using a variety of techniques, including solution-based NMR, ssNMR, AFM, STM, TEM and electrochemistry. We also have developed methods by which these Au NPs can be immobilized at carbon surfaces so they can be electrochemically addressed. These methods begin with oxidative immobilization of amino thiols or amino disulfides at carbon surfaces *via* attack of electrogenerated amine radical cations at the carbon surface. After that, the modified surface is exposed to a solution containing the Au NPs, which are immobilized due to interaction with the thiol or disulfide centers. Finally, we show electrochemical results that demonstrate the successful "wiring" of these Au NPs to the carbon electrode.

Progress Report

During the past year we have succeeded in adapting and scaling up the synthesis of $Au_{101}(PPh_3)_{21}Cl_5$ nanoparticles previously reported by Hutchison's group at University of Oregon.[3] In our hands, the reported synthesis gives relatively polydisperse material. Thus, we are working to modify the purification to give more monodisperse TPP-capped Au NPs. Also, we have modified several previously reported methods to synthesize small diameter citrate-capped Au NPs. We have characterized these two types of Au NPs using several techniques, including transmission electron microscopy (TEM), ^{31}P NMR (both solid state and liquid state), ^{1}H NMR (liquid state), thermogravimetric analysis
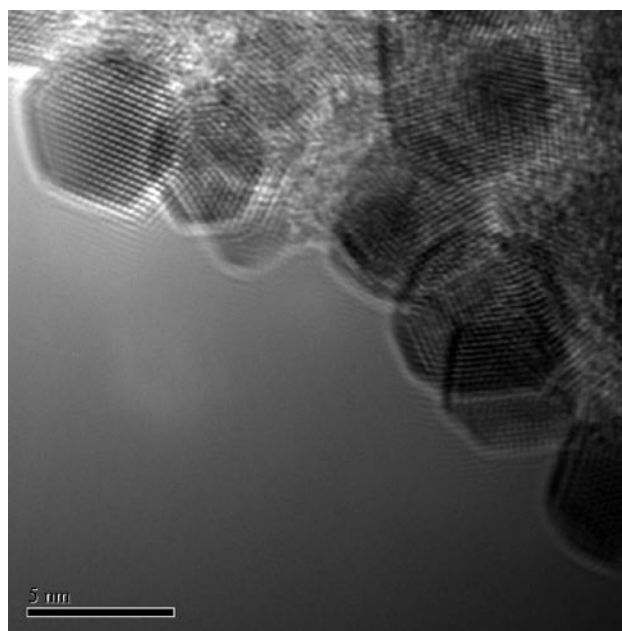

FIGURE 1. High resolution TEM image of "Au_{101}" NPs prepared as described in the literature.
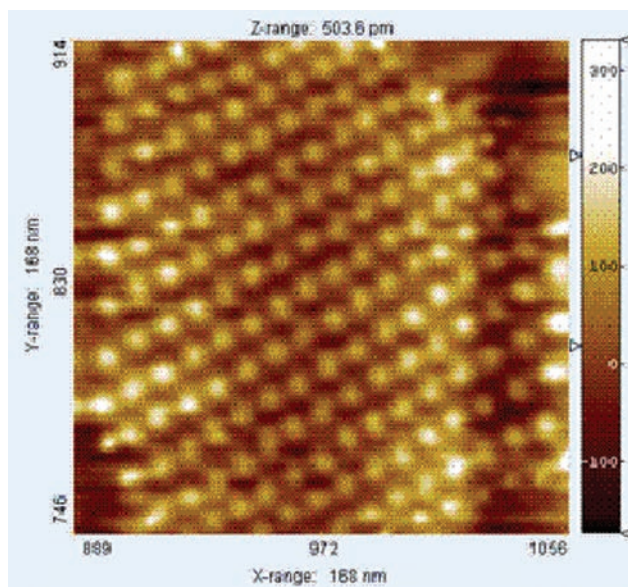
FIGURE 2. STM image of hexagonal array of "Au$_{101}$" NPs drop cast from CH$_2$Cl$_2$ solution onto HOPG. Pt/Ir tip; i = 0.5 nA, bias = 0.5 V.

(TGA), atomic force microscopy (AFM), scanning tunneling microscopy (STM) and electrochemistry.

The TEM image in Figure 1 shows that for the reported synthetic procedure the Au NP size is in the 4-6 nm range, considerably larger than in the original report. Thus, we refer to these as "Au$_{101}$" to emphasize that they do not have the size expected for a nanoparticle with a Au$_{101}$ core. These data also show the shape of the NPs, and show lattice fringes revealing the crystallinity of the NPs. We are analyzing these data to obtain histogram information on the size distribution of the NPs and how it is influenced by the details of the synthetic procedure. We also have developed a modification of the purification protocol that provides Au NPs with diameters in the range 1.5 - 2 nm.

We have used AFM and STM to image the "Au$_{101}$" NPs on HOPG surfaces. Interestingly, under STM examination we observe self-assembly of the Au NPs on HOPG substrates. Figure 2 shows a 168 nm x 168 nm AFM image of the TPP-capped "Au$_{101}$" nanoparticles drop cast onto a HOPG substrate from CH$_2$Cl$_2$ solution. As can be seen, the Au NPs self-assemble into a two dimensional hexagonal array with an interparticle center-to-center distance in agreement with the TEM data. We observe such assemblies over distances as large as half a micron. They are very stable and can be imaged for prolonged periods. The self-assembly and stability of such arrays is likely due to favorable interactions between phenyl rings on TPP adsorbates on adjacent nanoparticles.
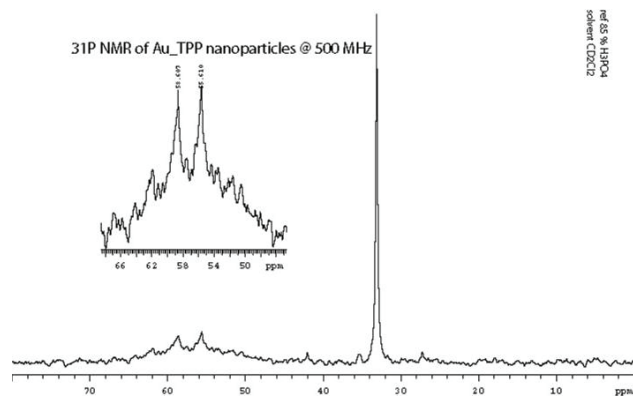

FIGURE 3. ^{31}P liquid state NMR of TPP-capped "Au$_{101}$" NPs in CD$_2$Cl$_2$.

We have used TGA to analyze the organic content of the Au$_{101}$(PPh$_3$)$_{21}$Cl$_5$ nanoparticles. Weight loss confirms the organic fraction to be 24%, which is in reasonable agreement with expectations based on the observed size range. We also have used NMR measurements to begin characterizing the NPs and capping agents at their surface. The ^{31}P NMR spectrum below shows a liquid state spectrum, with resonances at 56 and 59 ppm corresponding to the adsorbed phosphine capping agents. We also have obtained ssNMR data on this system that are currently being analyzed.

Our most recent work has involved preliminary attempts to immobilize the two types of Au NPs at carbon surfaces. We have used oxidative immobilization of amino thiols or amino disulfides at carbon surfaces *via* attack of electrogenerated amine radical cations at the carbon surface. These experiments have been carried out in both aqueous and non-aqueous solutions such as acetonitrile (ACN). Figure 4 shows an example of the oxidative immobilization of aminothiophenol (ATP) at a glassy carbon surface. Following immobilization of sulfur-containing linkers, the modified surface is exposed to a solution containing the Au NPs, which are immobilized due to interaction with the thiol or disulfide center. Electrochemical examination of these surfaces shows gold oxide formation and stripping, demonstrating that Au NPs can, indeed, be immobilized using this route.

We also have begun to examine the electrocatalytic behavior of these immobilized Au NPs toward O$_2$ reduction. Figure 5 shows the reduction of O$_2$ in unbuffered 0.1 M Na$_2$SO$_4$ at a glassy carbon electrode surface first modified with ATP and then with TPP-capped "Au$_{101}$". The figure also shows the control experiment in which an ATP-modified surface with no Au NPs is scanned over the same potential range
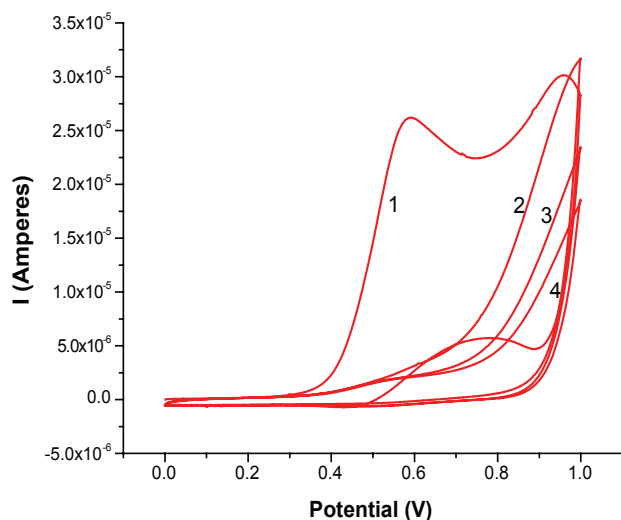
FIGURE 4. Cyclic voltammogram of ATP immobilization at a glassy carbon surface *via* oxidative immobilization. Scan rate - 0.1 V s^{-1}, 1 mM ATP in 0.1 M LiClO$_4$/ACN.
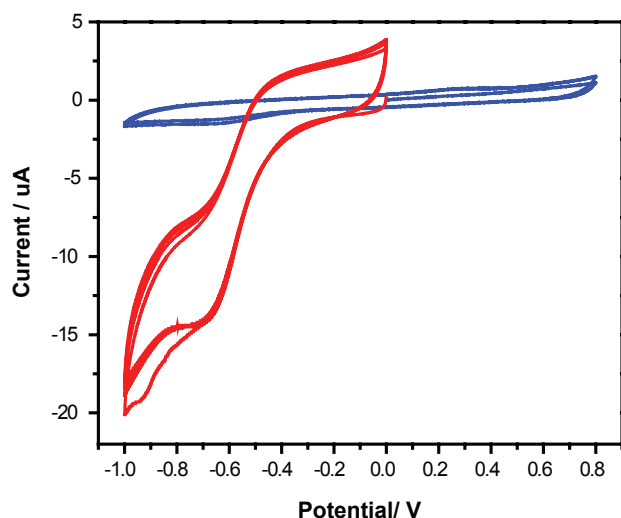

FIGURE 5. Cyclic voltammograms of a ATP-modified GC surface (blue - control expt) and a ATP/Au NP modified GC surface (red) in O$_2$-saturated 0.1 M Na$_2$SO$_4$. Scan rate = 0.1 V s^{-1}

in presence of O$_2$. As can been seen, there is clear evidence for O$_2$ reduction at the Au NP-modified surface. While the potential at which this reduction occurs is not sufficiently negative as to be interesting from an electrocatalytic perspective, these experiments

do demonstrate our ability to both immobilize Au NPs at carbon surfaces and to address these Au NPs electrochemically. We are investigating the origins of the relatively poor performance of the Au NPs in these experiments. There are many possibilities, including the size of the NPs, the presence of strong adsorbates at the Au NP surface (*i.e.* TPP) that may prevent the chemisorption of O$_2$, and others.

Future Directions

In the next year, we will accomplish three important goals. First, we will finalize a routine method to immobilize the phosphine-capped Au$_{101}$(PPh$_3$)$_{21}$Cl$_5$ nanoparticles at electrode surfaces so that we can more thoroughly characterize their electrochemical behavior as O$_2$ reduction catalysts. Second, we will implement ssNMR techniques that can be used to examine the adsorbates on Au NPs. One example of such an experiment will be to titrate thiols into the NP solution and use NMR to examine the displacement of one or more phosphine adsorbates. The objective is to controllably change the adsorbate number and composition in order to examine the influence of such changes on the electrochemical behavior of the adsorbates. Third, we will begin to use ssNMR methods to examine adsorbates at the surface of Au NPs immobilized on high surface area carbon substrates (*e.g.* C aerogels). This will require the development of sampling techniques for solid carbon materials.

References

(1)   Ross, P. N. In *Handbook of Fuel Cells - Fundamentals, Technology and Applications*; Vielstich, W., Lamm, A., Gasteiger, H. A., Eds.; John Wiley & Sons: Chichester, UK, 2003; Vol. 2, pp 465-480.

(2)   El-Deab, M. S.; Sotomura, T.; Ohsaka, T. *Electrochemistry Communications* **2005**, *7*, 29-34.

(3)   Weare, W. W.; Reed, S. M.; Warner, M. G.; Hutchison, J. E. *J. Am. Chem. Soc.* **2000**, *122*, 12890-12891.

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