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Deposition of platinum particles on surface-modified carbon ultramicroelectrodes

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Abstract

Nanoparticles are used as electrocatalysts due to their large surface area-to-volume ratios. Most studies of nanoparticle electrocatalysis are performed on collections of particles on a support, which represent ensemble average behavior influenced by spatial distribution of the nanoparticles. Therefore, recent emphasis has been placed on analyzing electrocatalytic behavior of single particles. The focus here is to develop carbon ultramicro- and nanoelectrode platforms for studying the electrocatalytic properties of single metal nanoparticles. Ultramicroelectrodes were prepared using chemical vapor deposition of carbon in pulled quartz capillaries. Electrode diameters were determined by cyclic voltammetry. Electrodes were modified using a soft nitriding technique to enable immobilization of platinum nanoparticles through reduction of H_2PtCl_6 using $NaBH_4$. Cyclic voltammetry was used to determine the presence of platinum particles through characteristic peaks associated with Pt oxide formation and reduction. Ultimately, these electrodes could be used to analyze single uncapped nanoparticles to understand the electrochemical properties of single nanoparticles.

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CHAPTER 1

INTRODUCTION

Background of Nanoparticles and Their Uses

Nanoparticles are particles that range from 1-100 nm in size. The shape, size, and composition of the particles can be tailored to perform specific tasks and facilitate reactions.[1]

Due to their small size and interesting properties nanoparticles are currently of interest in areas such as pathogen detection, drug delivery, tissue engineering, and MRI enhancement.[2] Their relatively large surface area-to-volume ratios make them well-suited as catalysts for various reactions as they have many active surface sites while requiring less raw material compared to bulk materials.

Metal nanoparticles have been studied extensively for their abilities to serve as catalysts for electrochemical reactions (i.e. electrocatalysts), such as those used in proton exchange[3] and polymer electrolyte[4] fuel cells. The reactions that drive low-temperature fuel cells are inefficient without the use of expensive platinum catalysts. By replacing the bulk platinum with nanoparticles it is possible to produce more cost-efficient fuel cells due to the reduction in the amount of materials needed.[5]

Analysis of Nanoparticles and Nanoparticle Collections

While many studies are focused on developing and applying different catalysts for fuel cell reactions,[6] optimizing these catalytic properties to enhance fuel cell efficiency can be challenging as most studies involving nanoparticles are typically performed on collections of particles deposited on larger conductive surfaces. Since nanoparticle collections are often heterogenous in size and shape, both of which affect electrocatalytic behavior,[7] the resulting electrocatalytic measurements represent an ensemble average and leads to loss of information. Factors related to the spatial distribution of particles, such as interparticle distance can also be widely varied in nanoparticle ensembles and are often difficult to characterize and control using electrocatalysis. These complications associated with measurements obtained from particle collections make it difficult to determine the important link between nanoparticle structure and electrocatalytic capabilities. This link is crucial to the development and optimization of nanoparticle electrocatalysts. For this reason, there has been a growing recent interest focused on the measurement of the electrocatalytic properties, such as the ability to catalyze oxidation reduction reactions, of single, isolated nanoparticles.

There are currently two electrochemical methods used to analyze the electrocatalytic properties of single nanoparticles: nanoparticle impact and single-nanoparticle immobilization. Nanoparticle impact analysis involves measuring the current at an ultramicroelectrode, an electrode with a radius less than 25 µm[8], with respect to time while the ultramicroelectrode is immersed in a suspension of nanoparticles.[9] Though these experiments can be performed using different methods, electrocatalytic behavior can be best studied by holding the electrode at a potential where the nanoparticle is capable of facilitating the reaction at that potential but the electrode is not. The collision of a single particle with the electrode surface results in a change in current that can be transient or permanent depending on how strongly the particle sticks to the surface or if the particle becomes deactivated. The magnitude of the spike- or step-shaped change in current (event) is related to particle size and electrocatalytic properties while the frequency of occurrence of such events is related to the concentration.[10]

Single Nanoparticle Studies

Single-nanoparticle immobilization measurements are performed by isolating a single particle on a nanoelectrode of size comparable to the particle so that the immobilized particle can be electrochemically characterized using voltammetry or other electrochemical methods.[11] Single metal nanoparticle immobilization has been performed through several methods, including direct adsorption, electrostatic adsorption, electrodeposition, and covalent binding[12] with varying materials used for the nanoelectrode platform. Sun et. al.[13] and Zhang et. al.[14,15] both used platinum ultramicroelectrodes to immobilize gold nanoparticles. However, platinum nanoelectrodes can also behave catalytically towards many of the same reactions, especially oxidation reduction reactions, that the metal nanoparticles can catalyze which can limit the application of this strategy and complicate analysis.

Mirkin et. al.[16] studied the electrocatalytic behavior of single gold nanoparticles toward the hydrogen evolution reaction by immobilizing them on carbon nanoelectrodes. The researchers demonstrated that a single citrate-capped gold nanoparticle could be directly adsorbed onto an unmodified electrode. They also showed that a gold nanoparticle could be alternatively immobilized via electrostatic or covalent attachment onto an electrode that was modified with a polymer layer via reduction of an aryl diazonium salt. Direct adsorption onto the unmodified electrode was unstable while the insulating properties of the polymer layer impeded electron transfer between the particle and the carbon electrode.

Use and Modification of Carbon Electrodes

The use of carbon electrodes as platforms for measuring the electrocatalytic properties of single metal nanoparticles holds great promise since carbon is often relatively inert towards many of the reactions catalyzed by metal nanoparticles. However, there is a need to explore other strategies for isolating single metal nanoparticles onto carbon nanoelectrodes.[17-19] Recently Liu et al.[20] reported a process for depositing highly electrocatalytically active metal nanoparticles onto various carbon black and mesoporous carbon support materials using soft nitriding which introduces nitrogen groups on the carbon surface. The group used a low-temperature urea pretreatment to enrich nitrogen-containing species on the surface of the carbon supports which enhances the support’s affinity for the metal nanoparticle precursors. Particles of Au, Pd, and Pt were then grown *in situ* onto the supports producing ultrasmall (< 2 nm) noble metal nanocatalysts that were ligand free and could be used for electrocatalytic reactions such as methanol oxidation.

The purpose of the research presented here is to apply the soft nitriding technique on carbon ultramicro- and nanoelectrodes prepared by chemical vapor deposition[21] to immobilize bare platinum particles. This research will hopefully lead to carbon electrode platforms that are easily produced, easily modified via nitriding, and able to attach a single uncapped metal nanoparticle for electrocatalytic studies, especially oxidation reduction where platinum is extremely useful.

CHAPTER 2

METHODS

Production of Carbon Ultramicroelectrodes by Chemical Vapor Deposition

For these experiments quartz capillaries (0.5 mm internal diameter, 1.0 mm outer diameter, 10 cm length) were pulled into pipettes using a laser-based pipette puller (P-2000, Sutter Instrument Co.) under the following conditions: Heat-850, Filament-4, Velocity-36, Delay-140, and Pull-50. A previously reported chemical vapor deposition procedure[22] was used to deposit carbon in the capillary pipettes. Briefly, the pipettes were clamped into a stand and attached to a container of camping gas (propane-butane 30:70 mixture) via tubing connected to the un-pulled end of the capillary. The tapered end of the pipette was placed in the path of an opposing flow of argon to provide and inert atmosphere, and while the propane-butane mixture was being passed through the pipette, a butane torch was used to heat the tapered end of the capillary for approximately twenty seconds. The presence of an orange glow inside the pipette was observed during heating, indicating that deposition was taking place, and successful deposition was confirmed by the appearance of a black carbon film within the capillary tube. A wire was then placed into the open end of the capillary, where it made contact with the surrounding carbon, in order to make contact with the electrochemical workstation.

Nitriding of CVD Electrodes

Some electrodes were suspended above 1 g of urea dissolved in 25 mL of distilled water which was heated at 100 °C for 1 hour in an attempt to modify the carbon surface with nitrogen containing groups. The electrode was then rinsed on the outside with ethanol. No tests were available to determine if nitrogen was present after nitriding.

Platinum Nanoparticle Attachment

Both nitrided and unmodified electrodes were then placed in 5 mL of 0.025 mg/mL chloroplatinic acid solution to which 2 mL of 0.025 M $NaBH_4$ was added and sonicated for 30 minutes. This reduction is expected to result in the formation of solid platinum particles. After sonication the electrodes were left in the solution for varying amounts of time including: 12 hours, 1 hour, 30 minutes and 15 minutes in order to determine if time after sonication was a factor in particle attachment. The electrodes were then rinsed with ultrapure water.

Electrochemical measurements

All electrochemical measurements were obtained using an Epsilon Electrochemical Workstation (Bioanalytical Systems, Inc.) with the working electrode lead connected to the carbon ultramicroelectrode and the counter/reference leads connected to an Ag/AgCl (3 M NaCl) reference electrode (Bioanalytical Systems, Inc.). To determine the electrode viability and size, electrodes were placed in a 1.0 mM ferrocene methanol (FcMeOH) in 0.1 M KCl solution and the potential was scanned from +50 to +450 mV vs. Ag/AgCl at a scan rate of 25 mV/s. Presence of platinum after reduction of chloroplatinic acid using $NaBH_4$ was evaluated by placing electrodes in 0.5 M H_2SO_4 and scanning the potential from -0.2 V to +1.4 V vs Ag/AgCl at a scan rate of 25 mV/s. In all voltammograms, oxidizing (positive) potentials are plotted to the right and currents associated with oxidation processes are presented as positive.

CHAPTER 3

RESUTLS AND DISCUSSION

Characterization of Electrode Size

After electrodes were prepared via chemical vapor deposition of carbon in quartz capillary tubes electrode size was determined from the diffusion-limited current measured using FcMeOH. The oxidation and reduction of diffusible redox probes like FcMeOH produce sigmoidal responses at disk shaped ultramicroelectrodes (Figure 1)[23]. This response can be used to determine the size of the electrode using the equation[24] $i=4nFDcr$ where i is the limiting current, n is the number of electrons involved in the reaction (1), F is the Faraday constant (96485 C/mol), c is the concentration in mol/cm^3 (1.0×10^{-6} mol/cm^3), r is the radius, and D is the diffusion coefficient of the redox probe[25] (7.8×10^{-6}cm^2/s).The limiting current was estimated based on the difference between the starting current of a cyclic voltammetry run and the maximum current. The calculated radius of the electrodes used in these studies ranged from 1.2-6.0 µm.

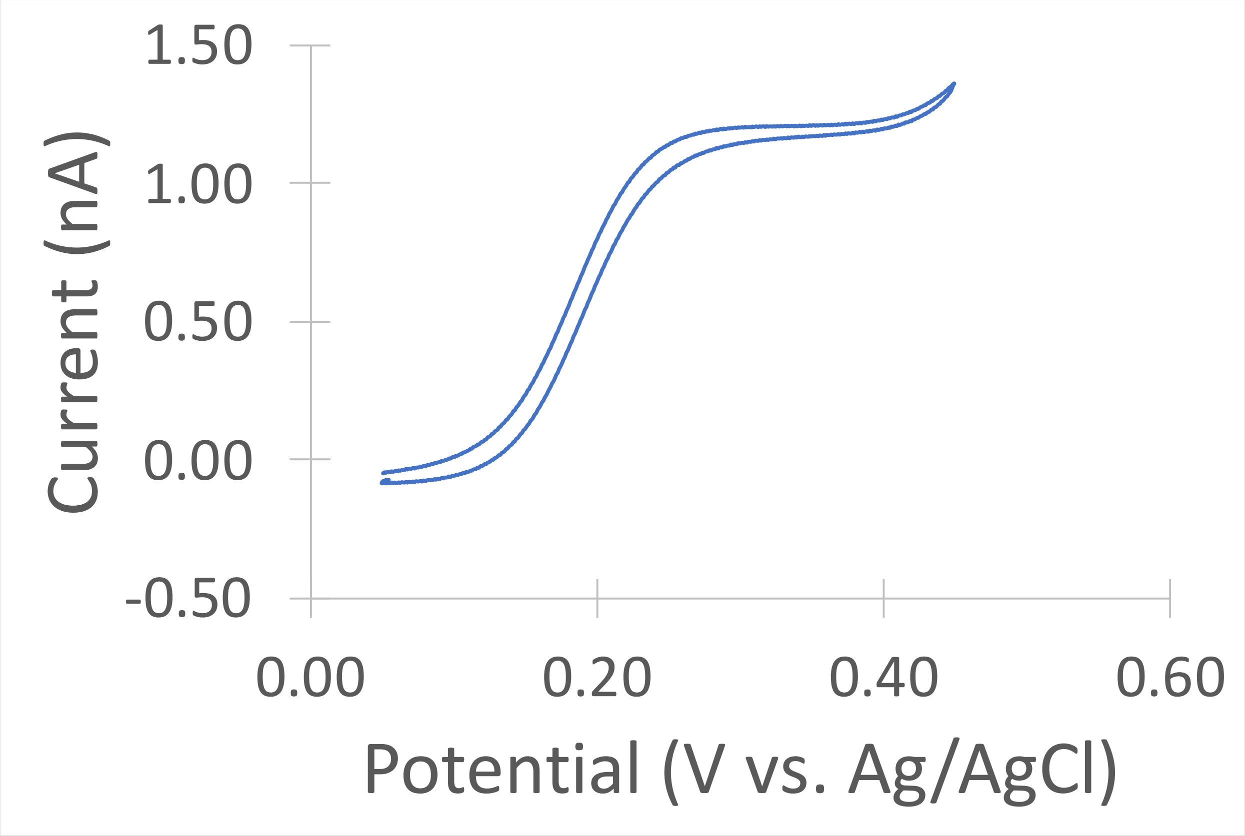


Figure 1: Cyclic voltammogram of carbon electrode prepared by CVD in 1.0 mM FcMeOH in 0.1 M KCl at 25 mV/s. Size determined to be 4.0 µm.

Characterization of Platinum Particle Deposition

Comparisons of pre- and post-particle deposition were based on cyclic voltammograms obtained in 0.5 M H_2SO_4 using similarly sized CVD carbon electrodes subjected to various Pt deposition times (Figures 2-4). Deposition of Pt using $NaBH_4$ reduction of chloroplatinic acid resulted in larger overall currents (~10-50x larger) compared to the current at 1.5 V on the pre-deposition voltammograms. This could indicate successful deposition of Pt as well as nanostructuring of the electrode surface which would increase the surface area of the electrode. Post-deposition voltammograms exhibit an oxidation peak around +0.55 to +0.65 V, as well as a broad reduction peak around +0.2 to +0.4 V, which are not observed in pre-deposition CVs.

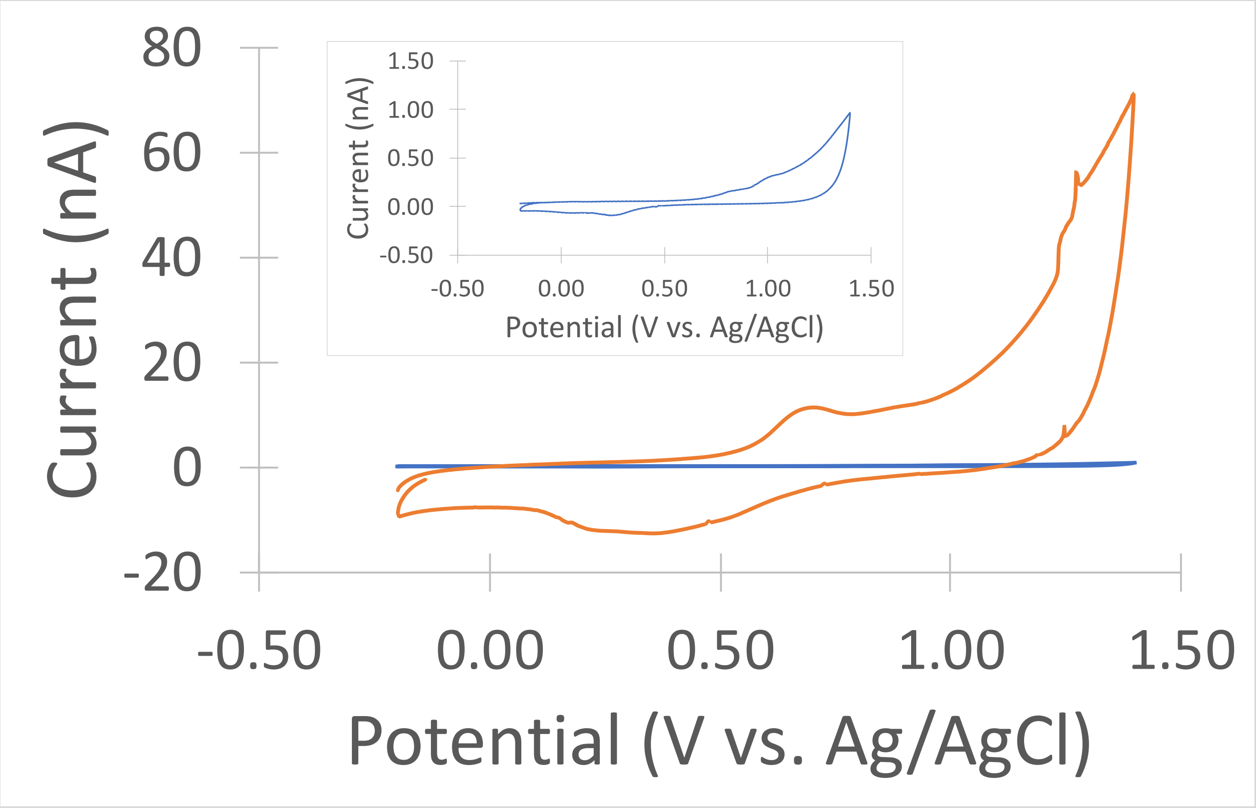
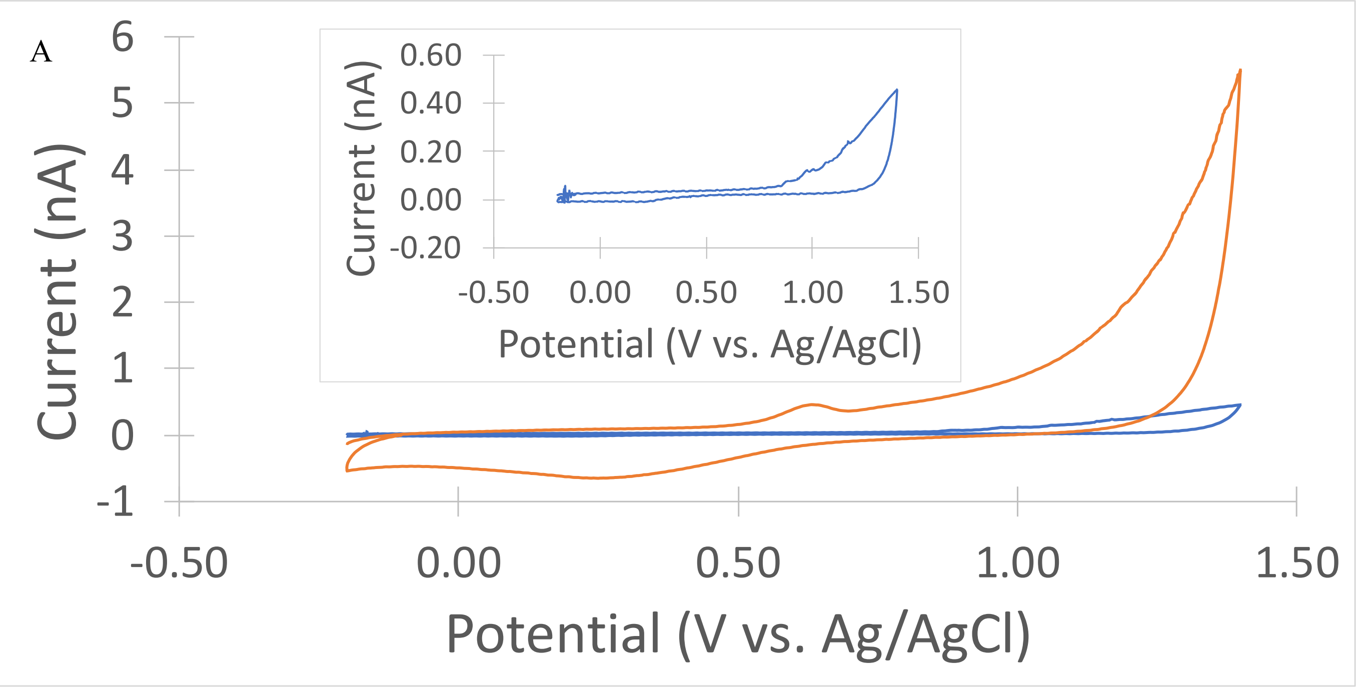


Figure 2: CV of nitrided 1.2 µm electrode in 0.5 M H_2SO_4 before (blue) and after (orange) attempted deposition of Pt particles via reduction of chloroplatinic acid by $NaBH_4$ for 12 hours. Inset shows pre-deposition response re-plotted on a smaller scale.



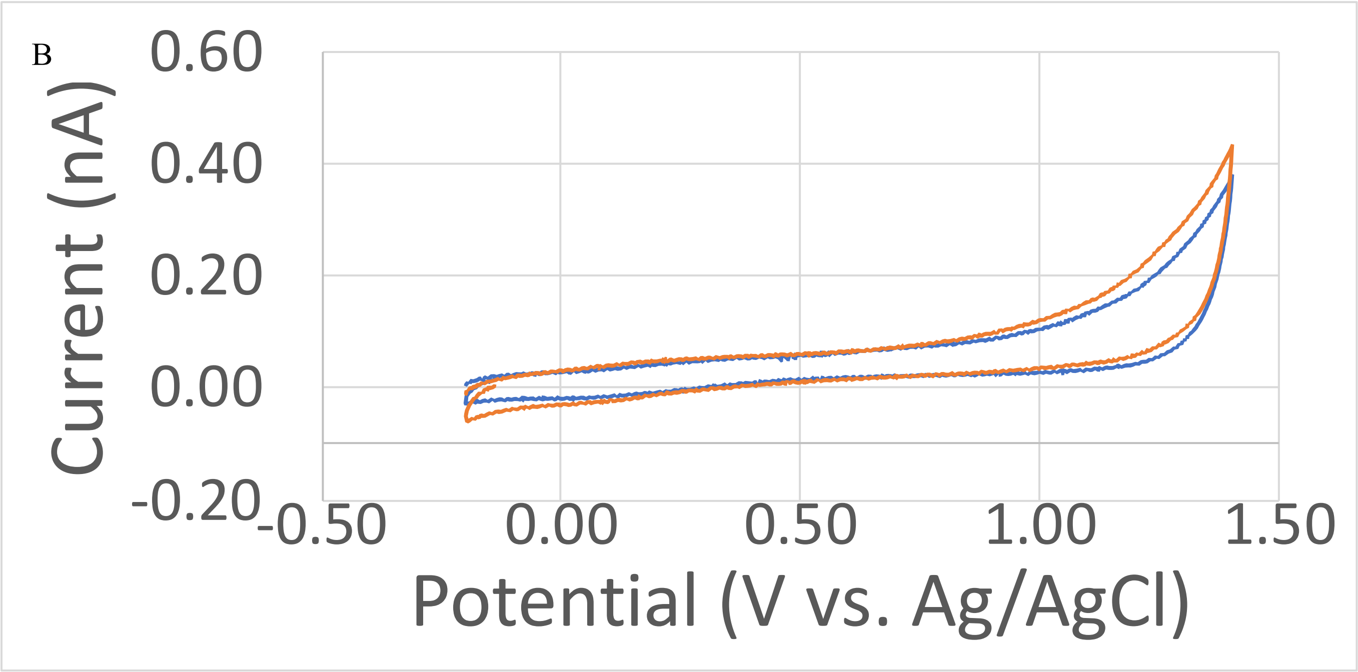


Figure 3: CVs of nitrided (A, top) 1.2 µm electrode and unmodified 6.0 µm electrode (B, bottom) in 0.5 M H_2SO_4 before (blue) and after (orange) attempted deposition of Pt particles via reduction of chloroplatinic acid by $NaBH_4$ for 30 minutes. Inset in A shows pre-deposition response re-plotted on a smaller scale.

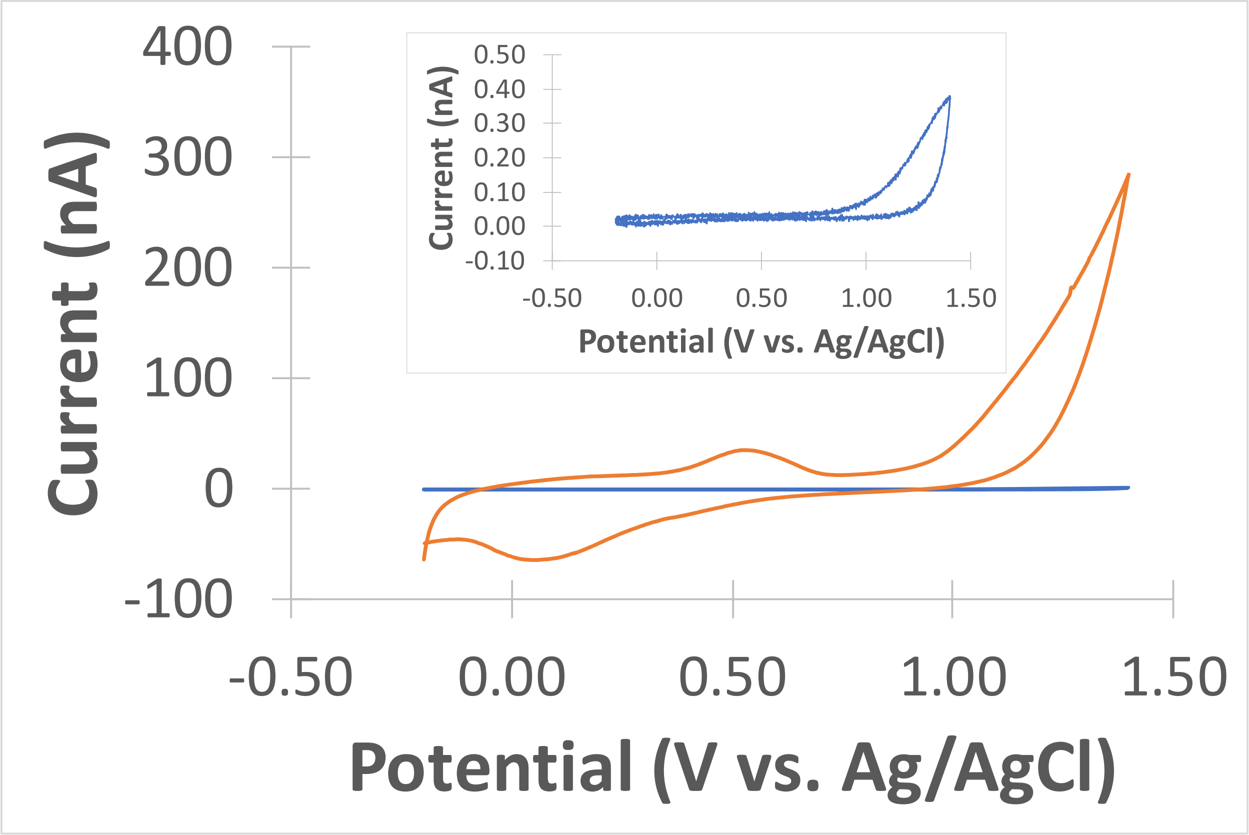


Figure 4: CV of nitrided 2.0 µm electrode in 0.5 M H_2SO_4 before (blue) and after (orange) attempted deposition of Pt particles via reduction of chloroplatinic acid by $NaBH_4$ for 15 minutes. Inset shows pre-deposition response re-plotted on a smaller scale.

Data Analysis

While there are clear differences between the pre- and post-deposition CVs' oxidation, reduction, and current size which would seem to suggest successful immobilization of Pt on the electrode surface, the peak positions and overall appearance of the post-deposition CVs are not consistent with the well-documented electrochemical behavior of platinum[26-28]. Literature values place oxidation as beginning at 0.5-.6 V, with reduction peaking at 0.4-0.5 V, which roughly coincide with the position of the data peaks. However, the reference peaks have a different structure than those obtained in these experiments. References show a broad oxidation peak that begins at ~0.5 V but which is centered at ~1.0 V. Also, the reduction peak, while still present at 0.4-0.5 V is typically a very sharp and narrow peak, unlike the broad peak seen in the data. While the presence of the peaks at the correct positions could indicate the presence of platinum on the CVD surface it is not definitive as the peaks are not the same shape as seen in most references.

While confirmation and characterization of active Pt on the CVD carbon surface should have been possible through the hydrogen adsorption region at ~0.1 V,[29] peaks in this region were not observed. Hydrogen adsorption occurs when hydrogen in solution is initially reduced and then oxidized by platinum. It is possible that there is no indication of hydrogen absorption due to absorbed impurities on the platinum surface. The use of an anodic pretreatment to produce Pt oxide and then reduction back to Pt should have been employed to clean the surface of impurities and promote hydrogen adsorption.[30] A second CV was run on each electrode after the initial measurements, none of these voltammograms showed any indications of peaks present. It is possible that a second run had an unexpected effect of removing the platinum particles or since it was a single run instead of the repeated cycles seen in literature, anodic pretreatment was not complete so characteristic peaks were not observed.

CHAPTER 4

CONCLUSION

Due to the shapes and positions of CV peaks in the data conflicting with those in the references, successful deposition of platinum could not be confirmed. In order to improve upon this work, future studies will need to address the extent and nature of nitrogen-containing groups introduced by nitrogen doping. This could be done by X-ray photoelectron spectroscopy (XPS) as previously reported[31,32]. XPS and electron microscopy should be used to analyze the surface for the presence of Pt and Pt particles. Presence of Pt particles could also be confirmed by measuring electrocatalytic behavior towards a reaction like oxidation of hydrogen peroxide. Verification of deposition of Pt on these carbon ultramicroelectrodes would open the door to single nanoparticle studies using similar carbon nanoelectrodes prepared by CVD.

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