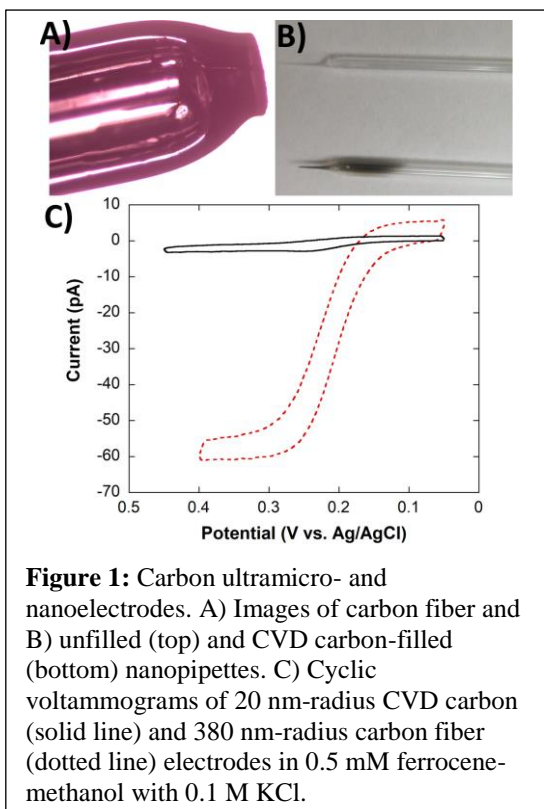


Catalytic and electrocatalytic properties of metal nanoparticles towards various reactions, including those involved in petroleum refining and emissions control, have been widely studied. However, most investigations have employed collections of particles deposited on bulk substrates. Factors related to nanoparticle distribution (e.g. interparticle distance, nanoparticle loading), which are often difficult or impossible to control and characterize, have been found to affect catalytic and electrocatalytic performance. Furthermore, measurements based on these systems represent the ensemble average behavior, and this presents challenges when trying to interpret the relationships between nanoparticle structure and function that are necessary to understand for predicting and optimizing catalytic activity. Recently, electrochemical techniques capable of evaluating single nanoparticles, which enable determination of electrocatalytic properties in absence of possible complicating aspects of nanoparticle dispersion, heterogeneity and ensemble averaging, have emerged. Our work is focused on measuring effects of surface ligands (capping agents) on electrocatalytic activities of metal nanoparticles through employing two single-nanoparticle electrochemical techniques: 1) nanoparticle impact and 2) nanoparticle immobilization.

The first funding period has yielded important progress towards both specific aims. Determining effects of capping agents on electrocatalytic activities of metal nanoparticles requires the production of metal nanoparticles of similar core size but with different ligands attached to the nanoparticle surface. Gold nanoparticles (AuNPs) have been produced using typical reduction of HAuCl_4 via NaBH_4 in the presence of organic capping agents cysteamine, glutathione and polyvinylpyrrolidone. Cysteamine- and glutathione-capped particles with similar sizes have been prepared, and we are working towards preparing and characterizing more particles of similar size. We are currently employing a nanoparticle impact method and also plan to image particles via transmission electron microscopy for more accurate particle sizing.

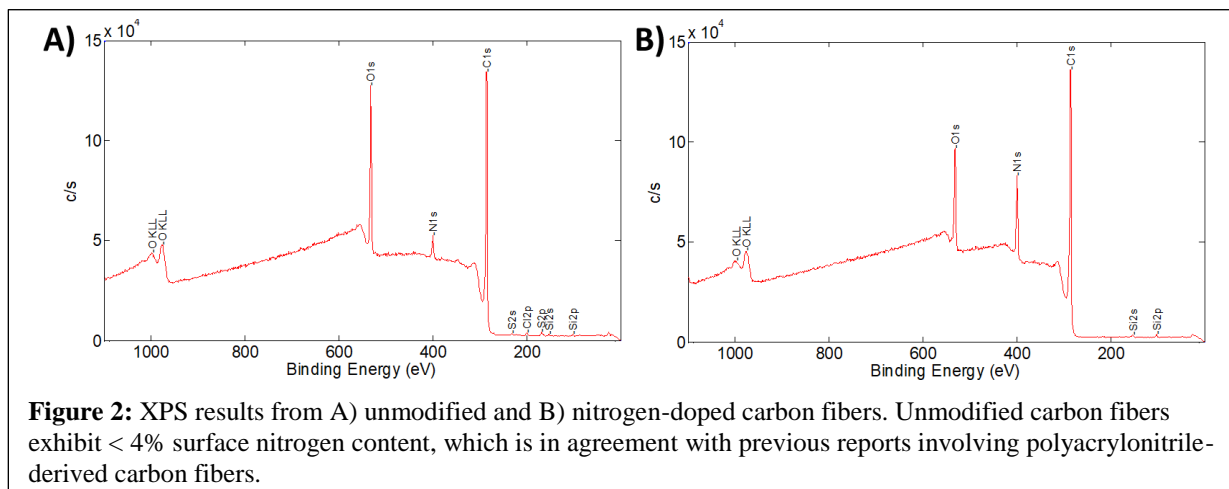


indicated that the nitrogen-doping process resulted in a $\sim 3.5x$ increase in surface nitrogen content compared to untreated fibers. Positions of N1s peaks also suggest a shift in the surface nitrogens from mostly amine/amide in nature to a slight excess of pyridinic groups upon nitrogen doping.

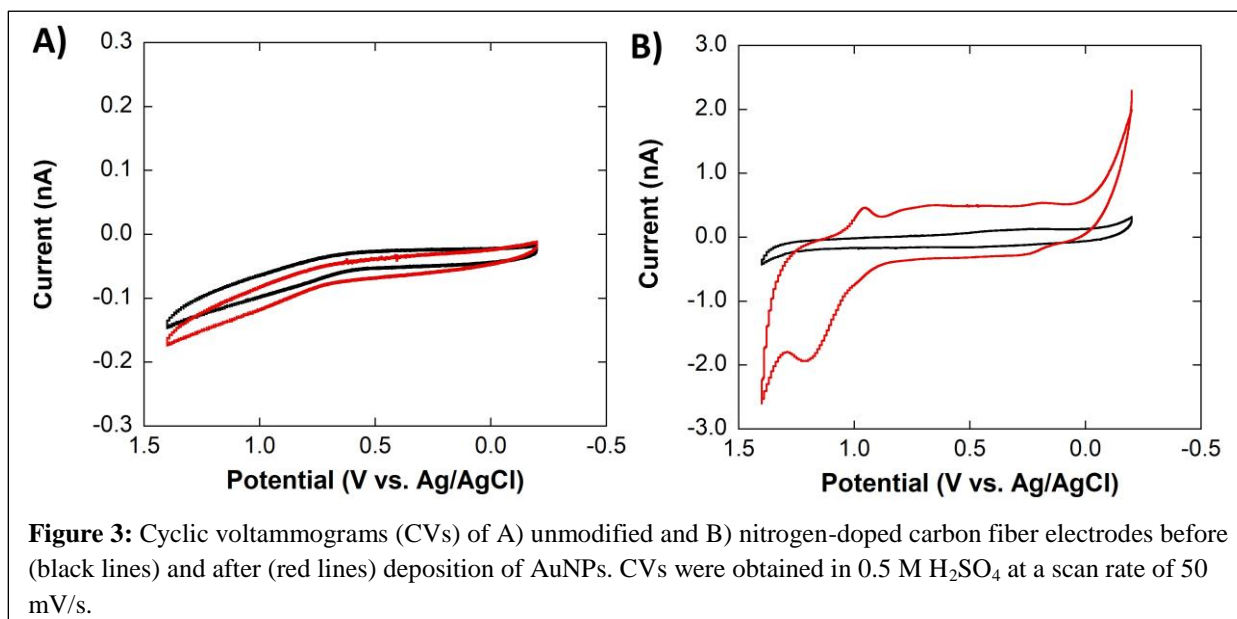
The increase in surface nitrogen content was found to facilitate immobilization of bare AuNPs through reduction of HAuCl_4 using NaBH_4 . Electrodes prepared from untreated carbon fibers did not exhibit any electrochemical

Determination of electrocatalytic properties of AuNPs through single-nanoparticle immobilization typically demands the use of nanoelectrodes that are similar in size to the nanoparticle of interest. We have focused our efforts during this initial funding period on preparing carbon nanoelectrodes due to the relative inertness of carbon towards many reactions that are promoted at metal nanoparticles. Ultramicro- and nanoelectrodes have been prepared using a laser-assisted pipette puller to 1) seal a $\sim 7 \mu\text{m}$ diameter carbon fiber in a glass capillary tube (Figure 1A) and 2) produce nanopipettes that are subsequently filled with carbon through chemical vapor deposition (CVD) by pyrolysis of hydrocarbon gases (Figure 1B). Various pulling parameters and processing strategies have been employed to minimize electrode size, which has been characterized through cyclic voltammetry in accordance with previous reports (Figure 1C).

While nanoparticle immobilization can be achieved through several means such as electrodeposition, direct or electrostatic adsorption, and covalent binding, we have been pursuing nitrogen-doping of carbon electrodes as recent literature has indicated such treatment can enable deposition of highly active bare metal nanoparticles on activated and mesoporous carbons. This strategy should facilitate immobilization of single bare and capped AuNPs as well as subsequent comparison of electrocatalytic activities. XPS analysis performed by Dr. Xu Feng and the Surface Analysis Laboratory of Virginia Tech



signal associated with gold even after more than 6 hours of deposition while nitrogen-doped carbon fibers showed clear evidence of electrochemically active AuNPs after less than 15 minutes of deposition (Figure 3). We plan to build on this progress by investigating effects of deposition parameters to immobilize and evaluate electrocatalytic properties of single particles.



This research has had significant positive impacts on both my career and on the students who have participated in the work. Results from these projects have already generated additional interesting research questions and related topics for our lab to explore – some of which have been included in a proposal that has been submitted. The work has also led to collaboration outside of our university and increased participation in our research program. ACS-PRF funds provided support for two undergraduates and two Master's students to work on this project over the summer. Students have gained experience in preparing ultramicro- and nanoelectrodes and become proficient in electrochemical and absorbance methods. Master's students involved in this project presented a poster at the regional ACS meeting in Charlotte, North Carolina, gave two oral presentations at departmental seminars, and two oral presentations at a university-wide research forum – with one presentation winning an award as the best overall oral presentation in natural sciences. Two Master's students involved in this endeavor successfully defended their theses that were both based on their work on this project and have continued on to chemistry PhD programs. Two undergraduates are continuing their research this fall with the intention of completing research theses for the chemistry honors program.