

Since recent reports have indicated that nitrogen-doping of carbon black enables deposition of highly electrocatalytic, ultrasmall (<2 nm) metal nanoparticles, we have focused our efforts on translating this method to carbon-based ultramicro- and nanoelectrodes in order to immobilize collections of metal nanoparticles and single metal nanoparticles for studies aimed at determining and comparing effects of capping agents in these systems. During the previous reporting period, we successfully modified carbon fiber ultramicroelectrodes (CF-UMEs) with surface nitrogen functionalities in a manner inspired by recently reported nitrogen-doping of carbon black, and we showed that nitrogen-doped CF-UMEs (N-CF-UMEs) similarly exhibited an improved propensity for immobilization of gold nanoparticles compared to unmodified CF-UMEs.

During this reporting period, we were able to translate the nitrogen-doping method to smaller carbon ultramicro- and nanoelectrodes prepared by a simple chemical vapor deposition (CVD) method. Nitrogen doping of carbon black by a similar method was previously reported to primarily involve reactions at oxygen-containing surface sites, and X-ray photoelectron spectroscopy (XPS) indicated a significant amount of oxygenated species on CVD carbon (~9% relative atomic surface concentration). However, confirmation of the presence of nitrogen groups on N-doped CVD carbon UMEs (N-CVD-C-UMEs) by XPS proved difficult because the nitrogen doping method only involves the surface layer of these small electrodes. Since N-doped carbon materials have previously been found to behave electrocatalytically towards the reduction of hydrogen peroxide, the response of N-CVD-C-UMEs in the absence and presence of H_2O_2 was compared to that of CVD-C-UMEs in order to verify success of the nitrogen-doping process on N-CVD-C-UMEs (**Figure 1**). Nitrogen-doping indeed enhanced electrocatalytic activity towards H_2O_2 reduction as indicated by the increase in reduction current and the +150 mV shift in onset potential using N-CVD-C-UMEs compared to CVD-C-UMEs.

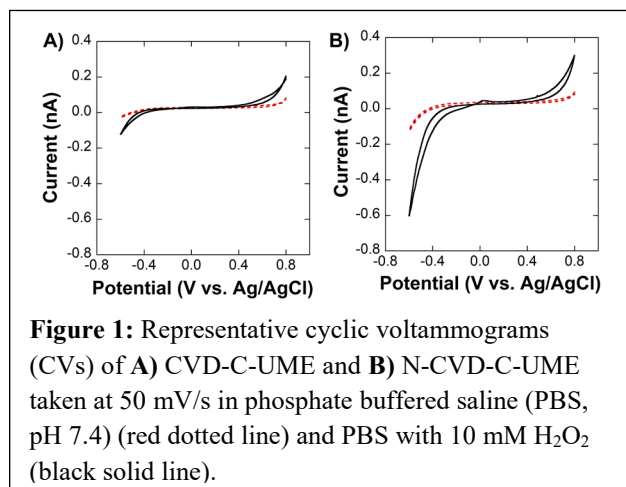


Figure 1: Representative cyclic voltammograms (CVs) of **A)** CVD-C-UME and **B)** N-CVD-C-UME taken at 50 mV/s in phosphate buffered saline (PBS, pH 7.4) (red dotted line) and PBS with 10 mM H_2O_2 (black solid line).

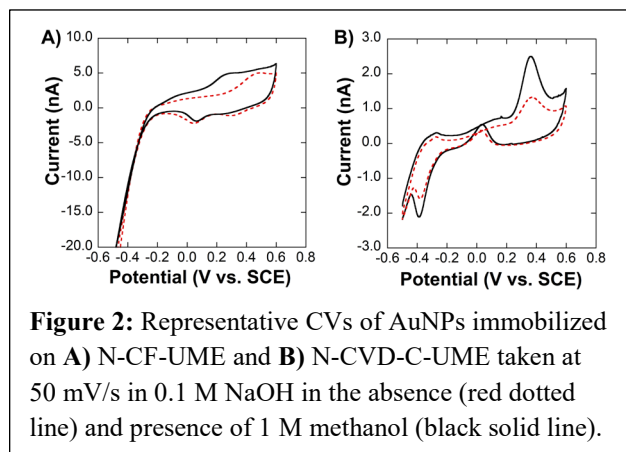


Figure 2: Representative CVs of AuNPs immobilized on **A)** N-CF-UME and **B)** N-CVD-C-UME taken at 50 mV/s in 0.1 M NaOH in the absence (red dotted line) and presence of 1 M methanol (black solid line).

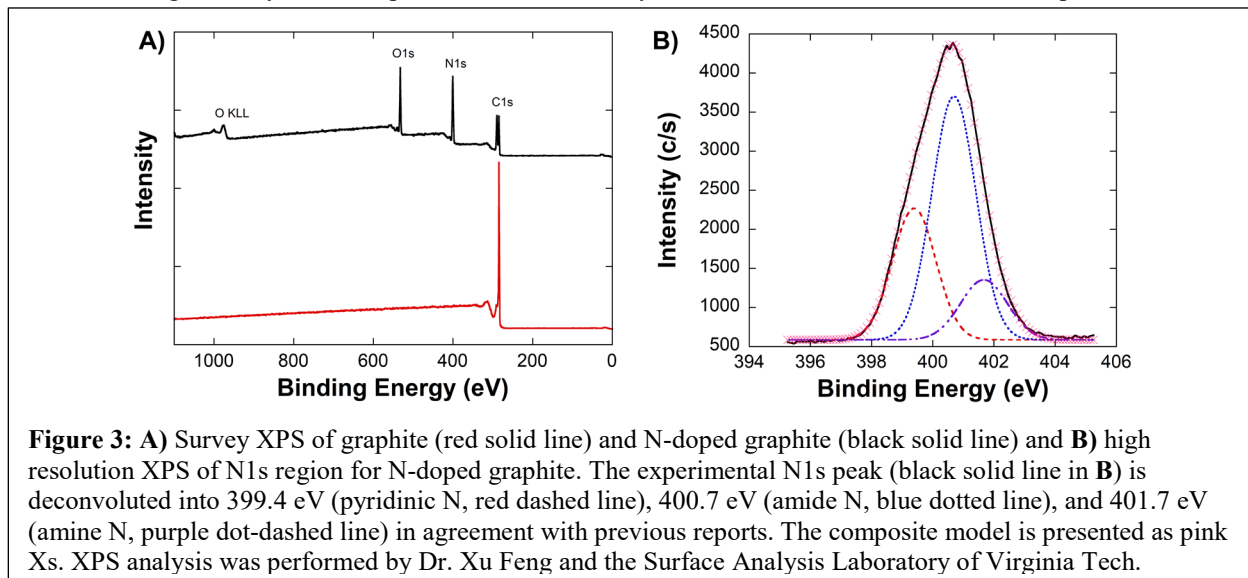
Gold nanoparticles (AuNPs), which were successfully immobilized on N-CF-UMEs during the previous reporting period, were deposited on N-CVD-C-UMEs during this reporting period by the same strategy. AuNPs on both types of electrodes demonstrated electrocatalytic behavior towards the oxidation of methanol (**Figure 2**). Since the same deposition method was employed for the immobilization of AuNPs on both N-CF-UMEs and N-CVD-C-UMEs, and a previous report demonstrated that the presence of nitrogen surface functionalities limited size and prevented overgrowth of AuNPs on other carbon materials, no differences in electrocatalytic behaviors of AuNPs on N-CF-UMEs and N-CVD-C-UMEs were expected. However, AuNPs immobilized on N-CF-UMEs exhibited a gold oxide formation peak (in the absence of methanol) at a slightly more positive potential than those deposited on N-CVD-C-UMEs. Furthermore, introduction of methanol resulted in a significant negative shift in oxidation peak potential for AuNPs on N-CF-UMEs that was not observed for AuNPs on N-CVD-C-UMEs, and AuNPs on CVD-C-UMEs exhibited a larger increase in relative electrocatalytic current for methanol oxidation than those on N-CF-UMEs. Disparities in electrocatalytic properties of AuNPs suggest there are differences in nanoparticle loading and possibly size on the different electrodes.

AuNP size was estimated by a recently reported electrochemical method based on ratio of charges associated with the reduction of the oxide layer that is

formed on Au surface atoms by electrochemical oxidation and the complete oxidative dissolution of AuNPs in the

presence of bromide to produce AuBr_4^- . Since these charges, which can be measured by CV experiments, are proportional to the surface area and volume of AuNPs, respectively, the ratio can be used to estimate the AuNP radius. Size estimates for AuNPs on both N-CF-UMEs and N-CVD-C-UMEs by this method ranged from 30 to 140 nm with the size of AuNPs on N-CF-UMEs showing a clear dependence on deposition time, and those on N-CVD-C-UMEs exhibiting greater variation with deposition time and pH of the deposition solution. Though sizes are significantly larger than ultrasmall (<2 nm) AuNPs reported on carbon black, electrochemical surface area-to-volume ratio is known to overestimate radius when surface coverage is high, and measured charge densities (~ 0.1 to $\sim 2.5 \text{ C/cm}^2$) confirm high surface coverage in this work. Research to translate deposition to smaller electrodes for single nanoparticle measurements is ongoing and should help determine if the apparent large AuNP size on UMEs is the result of overgrowth of AuNPs due to the nature of nitrogen functionalities or aggregation due to spatial distribution of nitrogen-containing sites. Imaging studies will also be completed in order to determine if large size estimated by electrochemical measurements is consistent with physical appearance.

Since sizing attempts indicated that less electrocatalytically active, larger AuNPs were deposited in these studies, we extended the nitrogen doping method to other carbon materials in an effort to better understand the process and improve deposition of metal nanoparticles on N-doped carbon electrodes. While the role of surface oxygenated species was previously described as crucial to the N-doping process, we surprisingly found that nitrogen doping of graphite was also successful despite the lack of surface oxygenated species. Nitrogen doping of graphite led to the introduction of large amounts of nitrogen ($\sim 33\%$) and oxygen ($\sim 19\%$) as determined by survey XPS (**Figure 3A**). High resolution scans indicated that a large portion of surface N atoms ($\sim 31\%$) could be indexed to pyridinic N with binding energy of 399.4 eV (**Figure 3B**). Pyridinic N has been linked to electrocatalytic activity towards reduction of H_2O_2 and high affinity for metal precursor ions necessary for immobilization of ultrasmall nanoparticles.



Support of the ACS-PRF has enabled me to build an active and vibrant research program with participation of undergraduates and Master's students as well as collaboration outside our university. The research has extended our understanding of carbon nanoelectrode fabrication/modification, nanoparticle deposition, and electrocatalysis in a way that has laid important groundwork for further investigation by provoking several additional interesting research questions we intend to address. Findings during this reporting period also contributed to a publication as we demonstrated the success of this nitrogen-doping strategy on carbon materials lacking oxygen-containing surface sites, characterized electrocatalytic properties towards H_2O_2 reduction (which we has also been using as a means to verify N-doping on N-CVD-C-UMEs) and applied of N-doped graphite towards detection of H_2O_2 . Two undergraduates and two Master's students participated in this research during the current reporting period. Both MS students presented posters on their work at the Southeast Regional Meeting of the ACS in Augusta, Georgia, gave oral presentations at departmental seminar, and successfully defended their theses. One MS student also gave an oral presentation at a university-wide research forum and obtained a position in industry after completion of the MS program. The other MS student continued on to a PhD program in chemistry after completion of the program. An undergraduate student who participated in the research during the previous reporting period completed an Honors thesis during this reporting period and enrolled in professional school, and another undergraduate who participated in research during the last two reporting periods is currently working on completing an Honors thesis.