ACS – PRF Annual Report (September 1, 2017 to August 31, 2018)

PRF # 55886-UR5

Project Title: ***In Situ Generated Two Dimensional Metal and Bimetallic Nanoparticle Catalysts***
Principal Investigator Name, Affiliation: ***Dr. Krisanu Bandyopadhyay, Department of Natural Sciences, University of Michigan-Dearborn***

Research Progress: In our present study, we have generated bimetallic AuPd nanoparticle (NPs) with varying Au:Pd mole ratio of 1:0, 1:0.5, 1:1, 0.5:1, and 0:1. Electrocatalytic activities of these systems have been evaluated for small alcohols and polyalcohol oxidation in alkaline medium. Bimetallic AuPd NPs assemblies are generated by simultaneous *in situ* reduction of $[PdCl_4]^{2-}$ with $[AuCl_4]^-$ ions bound to the Trimethoxysilylpropyl- polyethylenimine (TSPEI) functionalized surface. The multiple amine functionalities present at the polyethyleneimine (PEI) backbone of TSPEI can entrap both $[AuCl_4]$- and $[PdCl_4]^{2-}$) ions from solution through electrostatic interaction at a lower pH. Again in this synthesis, silicon and ITO have been used. The surface functionalization with trimethoxysilylpropyl modified polyethylenimine (TSPEI) has achieved followed by AuPd bimetallic NPs generation using 1×10^{-2} M $HAuCl_4$ and 1×10^{-2} M K_2PdCl_4 solutions which were made separately and mixed in different volumes to create the desired Au: Pd mole ratio in the final solution. After incubating the surfaces for 8 hours followed by rinsing with water and drying under a flow of argon, the surfaces with adsorbed ions were placed in a freshly prepared 0.1% (w/v) aqueous solution of sodium borohydride for 8 hours to generate the AuPd bimetallic NPs. Representative Atomic Force Microscopy (AFM) images shows nearly uniform AuPd NPs on silicon surface (Figure 1) after the final reduction step with the different Au:Pd mole ratio in solution. In this experiment, K_2PdCl_4 is used as Pd source. An apparent change in the morphology of the nanoparticles is observed with increasing the concentration of palladium ions, as obtained from analysis of a number of AFM images of different samples. AuPd bimetallic nanoparticle sizes are tabulated below.

Au:Pd Ratio	1:0	1:0.5	1:1	0.5:1	0:1
Particle Height (nm)	7.49	5.85	5.82	2.41	7.40

Preliminary results on electrocatalytic activity of PdNPs generated by borohydride reduction towards different alcohols are presented in Figure 1. A strong symmetric anodic oxidation peak during forward scan is the most noticeable feature in all of the electrocatalytic responses. In addition, all the votammograms show another anodic peak during reverse scan. This anodic peak in the reverse scan is attributed to the removal of the incompletely oxidized carbonaceous species formed in the forward scan. It is also known that accumulation of intermediate carbonaceous material on the catalyst surface leads to catalyst poisoning. Hence the ratio (I_f/I_b) of the forward anodic peak current density (I_f/I_b) to the reverse anodic peak current density (I_b), can be used to describe the catalyst tolerance of carbonaceous species accumulation. Low I_f/I_b ratio indicates poor oxidation of specific alcohol during anodic scan and excessive accumulation of carbonaceous residues on catalytic surface. High I_f/I_b ratio shows greater efficiency of the catalyst. Based on the I_f/I_b ratios presented below in table 1, it is very obvious that AuPdNP catalyst has shown that AuPd nanoparticle assemblies are showing catalytic activity towards small alcohols and polyalcohols.

Impact: The principal investigator and the undergraduate students are responsible for the execution of the present research project. Currently, they are pursuing the project and playing a major role in day to day research activities by performing different experiments for advancing the project forward. The undergraduate researchers are involved in mastering the experimental protocols, participating in interpretation and planning of experiments, co-author articles, and presenting their work in scientific meetings.

The present research is providing ample opportunity for undergraduate students to work in the emerging area of nano-structured catalyst. This study involves the use of AFM funded by NSF to PI at the University of Michigan-Dearborn and XPS facility in the Electron Microbeam Analysis Laboratory (EMAL) at the University of Michigan-Ann Arbor campus. Apart from the use of microscopy, electrochemical techniques like impedance spectroscopy and cyclic voltammetric measurements with corresponding data analysis is useful for students to understand the fundamentals of electron transfer process at the electrode and also to model the interfacial phenomena associated with it. This is an excellent opportunity for any undergraduate student to get research experience beneficial for future research endeavor. As a broader outcome, the present research helped the principal investigator to sustain a contemporary and challenging research program with active participation of undergraduates' at the Department of Natural Sciences, UM-Dearborn. Total 4 undergraduate students have worked on this project during last year. Among these, one student has graduated and three are currently in chemistry graduate program at UM-Dearborn. A manuscript is in preparation dealing with AFM, electrochemistry and zeta potential results. During August 2018, two undergraduate research students from PI's group presented a poster at the 256th American Chemical Society (ACS) National Meeting in Boston summarizing results from this current project. One of the students won the *Outstanding Student Poster Award* in the ACS Colloid and Surface Chemistry poster session.

Au:Pd Ratio	**Average Current Ratio i_f/i_b for each alcohol**	
	Methanol	**Ethanol**
1:0	0.18	8.45
1:0.5	3.48	0.98
1:1	4.32	1.10
0.5:1	1.42	0.75
0:1	7.60	4.11
Au:Pd Ratio	**Ethylene Glycol**	**Glycerol**
1:0	4.98	3.54
1:0.5	1.03	4.42
1:1	2.62	2.51
0.5:1	2.19	2.71
0:1	5.36	2.59