University of Victoria | Graduate Studies

Notice of the Final Oral Examination
for the Degree of Doctor of Philosophy

of

MAHDIEH ATIGHILORESTANI

MSc (Azad University Yazd Unit, 2008)
BSc (Azad University Yazd Unit, 2005)

“Design, Fabrication, and Electrochemical Surface Plasmon Resonance Analysis of Nanoelectrode Arrays”

Department of Chemistry

Friday, August 4, 2017
1:30 P.M.
Elliott Building
Room 226

Supervisory Committee:
Dr. Alexandre Brolo, Department of Chemistry, University of Victoria (Supervisor)
Dr. David Harrington, Department of Chemistry, UVic (Member)
Dr. Scott McIndoe, Department of Chemistry, Uvic (Member)
Dr. Rustom Bhiladvala, Department of Mechanical Engineering, UVic (Outside Member)

External Examiner:
Dr. Ian Burgess, Department of Chemistry, University of Saskatchewan

Chair of Oral Examination:
Dr. Jens Bornemann, Department of Electrical and Computer Engineering, UVic

Dr. David Capson, Dean, Faculty of Graduate Studies

Abstract

Recent advances in nanofabrication techniques have opened up new avenues and numerous possible applications in both nanoscale electrochemistry and analytical nanoscience by enabling the fabrication of reproducible nanoelectrodes with different new geometries. Nanoelectrodes exhibit advantages including enhanced mass transport, higher current densities, improved signal-to-noise ratios, and lower ohmic drop. In this dissertation, the use of nanoelectrodes in the electrochemical response properties investigations or in the spectroelectrochemical studies is the unifying factor among all the chapters. First (in chapter 4), we presented a direct comparison between the electrochemical characteristics of two finite nanoelectrodes arrays with different geometries: 6 × 6 recessed nanodiscs and nanorings microarrays. Using computational methods, it was demonstrated that the electrode geometry's parameters have a drastic influence on the mass transport properties of the nanoelectrodes. The results presented here are the first combination of experimental and numerical studies that elucidate the transport on nanoring electrode arrays. The comparison of the electrochemical behavior between nanostructures using full 3D simulations is also unique.

Second, we have provided a comprehensive numerical study on the redox cycling performance properties of a 6 × 6 recessed nanorings-ring electrode array configuration. The simulation results were in good agreement with the experimental data. After validating the model against experiments, a comprehensive computational investigation revealed avenues to optimize the performance of the structure in terms of geometric parameters and scan rates.

The second half of this thesis is comprised of the spectroelectrochemical studies. The combination of surface plasmon resonance with electrochemistry presents new paths to investigate redox reaction events at the electrode surface since it brings an additional dimension to the classical electrochemical approaches.

Third, we have reported a novel active plasmonic device based on a new switching mechanism for the nanohole electrodes array to bridge between photonics and

electronics at nanoscales. The inner surfaces of the nanohole electrodes in the array were coated with an electroconductive polymer, polypyrrole, (PPy). Then, it was shown that light transmitted through the PPy- modified nanohole electrodes can be easily tuned and controled by applying an external potential. We were also able to switch on and off the transmitted light intensity through the modified nanohole arrays by potential steps, demonstrating the potential of this platform to be incorporated into optoelectronic devices.

Finally, we have fabricated larger area plasmonic periodic nanopillar 3D electrodes using a rapid, high-throughput, and cost-effective approach: the laser interference lithography. Then, the electrochemical behavior of these electrodes was investigated both experimentally and computationally. The properties were ‘compared with a flat electrode with an equivalent geometric area. Afterward, we have successfully probed the changes in the concentration of a reversible redox pair near the electrode surface induced by various applied potentials, in an *in-situ* EC-SPR experiment.