

# NanoWestern



Western  
Science

Winter 2012



Dear Users of the Western Nanofabrication Facility,

It is with immense pleasure that I have accepted in July 2011 to lead our Nanofabrication Facility at Western University. Our facility offers unique access to techniques for fabricating a wide range of micro and nano structured materials and surfaces with the goal to design, fabricate and tune functional devices for a variety of application ranging from photonic waveguides, microfluidics, optical sensors as well as many other applications and was one of the decisive reasons for me to join Western. More specifically, we can highlight our fabrication expertise in focused ion beam technology and electron beam lithography, both which are recognized in Ontario and attract many academic and industrial users beyond Western. My vision of the Nanofabrication Facility is to make the choice of expanding our fabrication capabilities rather than its characterization possibilities. Our partner, Surface Science Western, has expertise in characterization and offers multiple unique techniques ranging from high spatial resolution XPS, atomic force microscopy and optical microscopy. Techniques that are complementary resources to the Nanofabrication Facility.

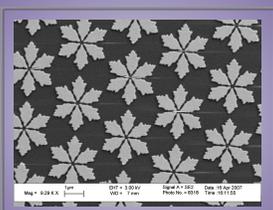
The Nanofabrication Facility, funded in 2001 and opened in 2004, is now reaching the 10 year threshold and it is becoming critical to offer the latest cutting-edge fabrication capabilities and to upgrade some of our key technologies. With the support of the Faculty of Science, and together with 9 co-principal investigators, I am in the process of applying for the last round of Canada Fund for Innovation-Leading edge fund, with the desire to acquire new technologies such as Nanoimprint Lithography to prepare large surfaces with nanometric size devices as needed in the fabrication of microfluidic or photovoltaic devices. Reactive ion etching processes and modern metal evaporation are needed urgently to replace older donated instrument that are more than 20 years old. The upgrade of our FIB and electron beam lithography are critical as we must provide the best fabrication tools if we wish to maintain our excellence in the fierce competition of nanofabrication and its application to plasmonics, optofluidic sensors or molecular spectroscopy in the next decade.

The daily operation of the facility has also been improved to promote the use of some instruments to a larger number of scientists at a lower cost. I have initiated the possibility to acquire bulk time on one of our scanning electron microscopes that can be used for high resolution imaging, as well as electron beam lithography. The associated entrance fee for just SEM imaging has also been suppressed, reducing the cost of the field emission SEM LEO 1530 to \$1400 for 60 hours when used at specific times of the week. This new operating scheme, started in December, has already attracted new groups to use our facility who may soon realize the full potential of the facility for their research projects.

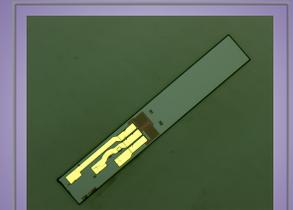
Beyond the activities of the Nanofabrication Facility, the faculties of Science and Engineering together with our Research and Development Services have agreed that Western becomes a founding member of the Nano Ontario network ([www.nanoontario.com](http://www.nanoontario.com)). I will therefore represent Western's excellence as a board member of this network to ensure that our visibility in nanoscience and nanotechnology will always be at the highest level. The next Nano Ontario conference will be held in the fall of 2012 at Waterloo and I am sure that Western's talent will be extensively represented at this event.

In conclusion, I strongly believe that the Western Nanofabrication Facility offers many possibilities and advantages over other competing facilities in Ontario due to its easy access, the quality of its training and the possibility to perform service work at a competitive price. Lastly, the success of the Nanofabrication Facility is also the result of the skills and expertise of Dr. Todd Simpson and Tim Goldhawk who are always passionate about solving new challenges and will be glad to answer your fabrication needs.

Fran ois Lagugn -Labarthe



Western Nanofabrication Facility  
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# Nanostructured Silver Surfaces and Their Properties in the Presence of Organophosphonates

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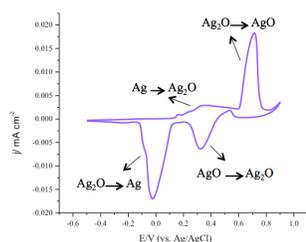
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In recent years, synthesis of silver nanoparticles has attracted significant attention due to applications in catalysis, water treatment, medicine, bioengineering, textile engineering, electronics and optics [1]. Various methods are known for the formation of silver nanoparticles of various shapes and sizes [1]. However, these methods come with certain drawbacks, for instance, the need for organic solvent, chemical stabilisers, heating, deaeration, etc. Due to the unique physical and chemical properties of nanoparticles, potential applications as part of electrochemical sensors were explored [2,3]. The benefit of using electrochemical analysis methods in comparison with other detection methods is the low cost, the ease of use, accuracy, reliability, less power requirement and the ability for miniaturization of the device [3].

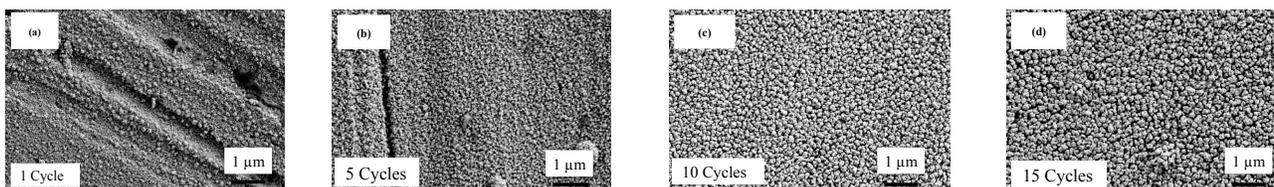
In the current study, we explore the electrochemical behavior of silver surfaces and report the formation of nanostructured silver surfaces under basic conditions in the presence of electrochemical cycling. The surfaces are studied by scanning electron microscopy (SEM) and our studies show a clear correlation between duration of electrochemical cycling, base concentration, and size of the nanostructured grains on the surface. Here we also explore the behavior of this surface to the presence of diethylcyanophosphonate (DECP), a mimic for the nerve agent Tabun. This compound hydrolyzes to release cyanide ions, which may lead to changes in the surface morphology. Studies with cyanide ions are conducted as a comparison.

## Preparation of Ag Nanostructures



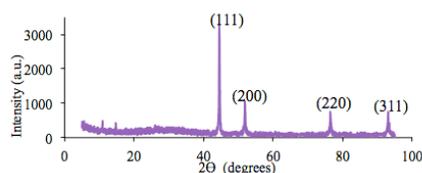
**Figure 1.** Left) The Ag foil appearance after 15 CV cycles in and right) A typical cyclic voltammetry scan of Ag foil in a solution of 8 M KOH at a scan rate of 0.15 V s<sup>-1</sup> in a potential range of -0.5 and 0.9 V vs. Ag/AgCl. On the anodic sweep peaks are observed due to the oxidation of Ag to the Ag (I) and Ag (II) oxides. On the cathodic sweep, these oxides are reduced back to Ag (0) and redeposit as Ag nanostructures.

## Surface Morphology

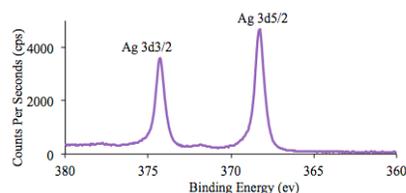


**Figure 2.** SEM study of the effects of electrochemical cycling of the silver foil in a potential range of -0.5 and 0.9 V vs. Ag/AgCl at a scan rate of 0.150 mV s<sup>-1</sup> at a supporting electrolyte concentration of 8 M KOH. The grain size increases with increasing electrochemical cycling (frames a to d).

## Characterization

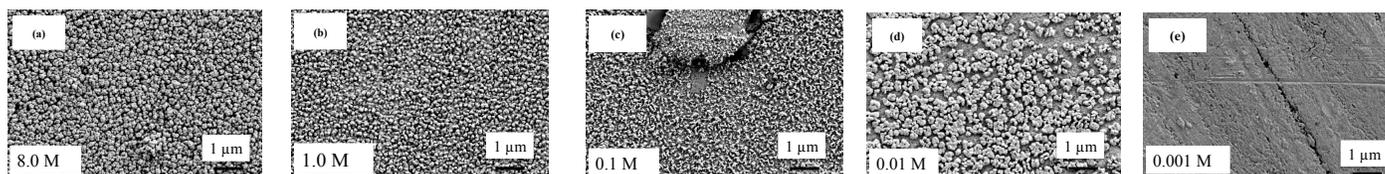


**Figure 3.** XRD pattern of the deposited Ag NSs on the surface of Ag foil formed by electrochemical cycling. The XRD pattern of the material exhibit 2θ values of 44.5, 51.9, 76.4 and 93.0 corresponds to the planes (111), (200), (220) and (311), respectively, of face centered cubic silver



**Figure 4.** XPS of the deposited Ag NSs on the surface of Ag foil shows signals at binding energies of 368.3 and 374.0 eV, characteristic for the Ag 3d<sub>3/2</sub> and 3d<sub>5/2</sub> signals of Ag (0).

## The Effect of KOH Concentration on Ag nanostructure Morphology



**Figure 5** SEM study of the effects of supporting electrolyte concentration on the surface morphology of the deposited Ag NS film. Shown are the results after 15 CV cycles in a potential range of -0.5 and 0.9 V vs. Ag/AgCl at a scan rate of 0.150 mV s<sup>-1</sup> in different KOH solution concentration as the supporting electrolyte (frames (a) to (e)). The grain size at 1.0 M KOH is clearly smaller compared to the 8.0 M KOH solution. Lowering the concentration of KOH further results in a less compact Ag NS film being formed. Particles are spaced out more and the silver underlayer is clearly visible. At a concentration of 0.001 M KOH, no significant accumulation of Ag NSs was observed.

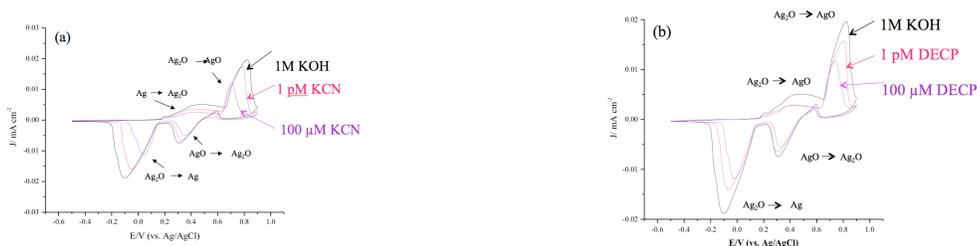
**Table 1.** The nano particle sizes (nm) and their standard deviation for different concentrations of KOH. There is no correlation between concentration and particle size. With increasing the CV cycles the particle size increase due to particle fusing.

CV SCAN NUMBERS	8 M KOH	1 M KOH	0.1 M KOH	0.01M KOH
1	31 ± 9	50 ± 20	47 ± 15	-
5	49 ± 15	57 ± 18	64 ± 18	-
10	63 ± 20	60 ± 15	64 ± 20	-
15	89 ± 27	69 ± 22	82 ± 24	152 ± 48

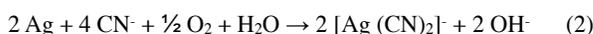
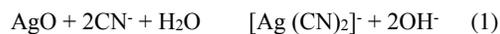
### Effect of DECP on Ag Nanostructure Electrochemistry and Morphology



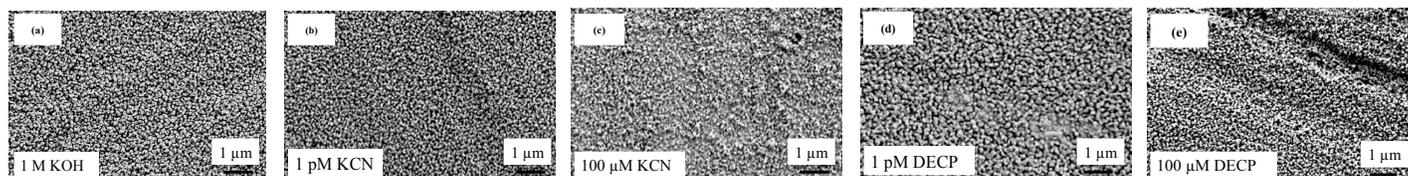
**Scheme 1.** Chemical structures of a) Tabun and b) diethyl cyanophosphonate (DECP).



**Figure 6.** Electrochemical behavior of Ag exposure to a) KCN b) DECP in 1M KOH at a scan rate of 100 mVs<sup>-1</sup> in a potential range of -0.5 and 0.9 V vs. Ag/AgCl. Note that for CN<sup>-</sup> and DECP addition, the peak intensities decrease. This is rationalized by the passivation of the silver surface by CN<sup>-</sup> ions, decreasing the anodic peaks. The cathodic peaks decrease in intensity due to the dissolution of the material as [Ag(CN)<sub>2</sub>]<sup>-</sup>.



Chemical reactions between AgO (1) and Ag (2) with CN<sup>-</sup> in cathodic wave



**Figure 7.** SEM images of the nanostructure silver surfaces as a function of KCN and DECP addition. Images were recorded after a total of 15 electrochemical cycles in the range of -0.5 and 0.9 V vs. Ag/AgCl at a KOH concentration of 1.0 M and a scan rate of 100 mV. a) shows the SEM image of a Ag surface exposed to KOH only and the formation of the nanostructured Ag film; b) addition of KCN (1 pM) causes significantly smaller grains; c) increased concentration of KCN (100 μM). The grains are smaller and less evenly distributed across the surface; d) DECP (1 pM) addition affects the grains; e) at a DECP concentration of 100 μM the surface is very heterogeneous and pitting can be seen on the surface due to dissolving Ag NSs.

### Conclusion

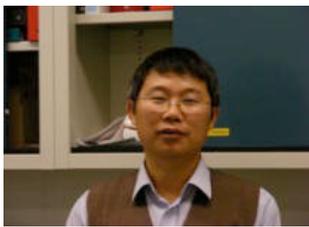
- 1- A nanostructured Ag surface has been prepared by electrochemical cycling in a potential range of -0.5-0.9V vs Ag/AgCl in KOH solution.
- 2- This surface morphology is affected by KOH concentration and by the number of electrochemical cycles. Increasing electrochemical cycling will increase grain size and aggregation on the surface.
- 3- Ag nanostructured surface is sensitive to the addition of cyanide ions.
- 4- Cyanide and DECP negatively affects the growth of the Ag grains.
- 5- At high cyanide and DECP concentrations pitting is observed and the Ag NSs start to dissolve.

### References

- [1] R.A.Khaydarov, R.R.Khaydarov, O.Gapurova, Y.Estrin, T.Scheper, *J.Nanopart Res*, **2009**, 11, 1193-1200.
- [2] X. Luo, A. Morrin, A.J. Killard, M.R. Smyth, *Electroanalysis* **2006**, 18(4), 319-326.
- [3] F.C. Campbell, R.G. Compton, *Anal. Bioanal. Chem.* **2010**, 396, 241-259.

### Acknowledgement

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# Film Formation and Conversion on Carbon Steel and Stellite-6

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Carbon steel and Stellite-6 are important nuclear material to make feeder pipes, ball bearings in the fuelling machine in CANDU® (CANada Deuterium Uranium) reactor. Corrosion of nuclear material is important for the performance and safety of nuclear reactor. Understanding the corrosion of nuclear material is a complex challenge. Corrosion kinetics are controlled by the nature of the material and the environment in which it resides including the aqueous redox chemistry at the metal surface and the physical and chemical nature of the metal surface or oxide film. In many environments of interest, particularly those associated with the nuclear industry, the presence of high energy, ionizing radiation can dramatically affect the water redox chemistry. This occurs because ionizing radiation decomposes water into a range of redox active species (e.g., •OH, H<sub>2</sub>O<sub>2</sub>, O<sub>2</sub>, •O<sub>2</sub><sup>-</sup>) whose concentrations evolve with time. Our present studies are performed to understand film growth and conversion on nuclear material as a function of radiation, pH, temperature, ionic strength and dissolved additives.

## Surface characterization on nuclear material at Western Nanofab

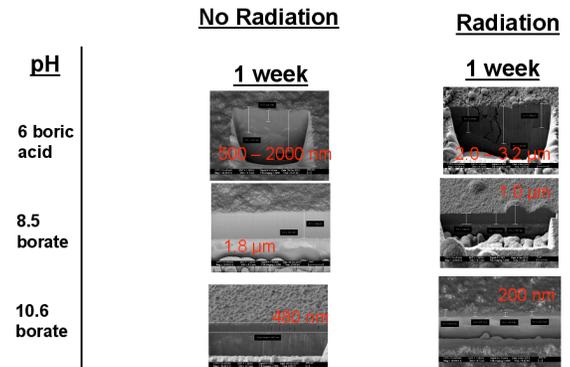
A LEO 1540XB SEM/FIB in Nanofab lab was used in the high-resolution mode to examine the morphology of corroded nuclear material coupon (Carbon steel and Stellite-6) surfaces. After examination by SEM, selected locations on the coupon surfaces were subjected to a cross-sectional cut through the surface film and into the underlying metal using a focused ion beam (LEO 1540XB). A thin layer of Pt was deposited on the coupon surface for demarcation and contrast for SEM imaging. An attempt to characterize the oxide growth as a function of time and solution pH for all systems was carried out through cross-section analysis. The oxides formed on carbon steel in pH<sub>25°C</sub> 10.6 and 8.5 borate solutions for one week are uniform compact oxides as shown in Figure 1, which is believed to be grown by a solid-state process, compared to the more porous oxides grown at pH<sub>25°C</sub> 6 in borate solutions in Figure 1. Film thickness decreased with pH whether under no radiation and radiation condition. Further more discussions were given in the publication [2]. Influence of irradiation on the film growth on carbon steel is dependent on pH of solution.

## Summary

Series factors influencing the film formation on nuclear material have been carrying out now. Variation in system temperature and pH affect the rates of oxide film growth and dissolution on nuclear material.

## Scientific Outputs resulting from the work

1. K. Daub, X. Zhang, L Wang, J.J. Noël, J.C. Wren, Oxide Growth and Conversion on Carbon Steel as a Function of Temperature Over 25 and 80°C Under Ambient Pressure, Accepted in *Electrochimica Acta*.
2. K. Daub, X. Zhang, J.J. Noël, J.C. Wren Film Growth on carbon steel at 150 °C, to be submitted.
3. Daub, K., Zhang, X., Noël, J.J. & Wren, J.C., "Gamma Radiation-Induced Carbon Steel Corrosion", Corrosion Issues in Nuclear Waste Storage: A Symposium in Honor of the 65th Birthday of David Shoemsmith: ECS transactions Vol. 33, Las Vegas, NV, October 10-15 (2010).
4. Daub, K., Zhang, X., Noël, J.J. & Wren, J.C., "A Comprehensive Study of Gamma-radiation Induced Corrosion of Carbon Steel", 8th International Radiolysis, Electrochemistry & Materials Performance Workshop, Quebec City, QC, October 8 (2010).
5. Daub, K., Zhang, X., Noël, J.J. & Wren, J.C., "Surface Analytical Study of Gamma-Radiation Induced Carbon Steel Corrosion", Nuclear Plant Chemistry Conference (International Conference on Water Chemistry of Nuclear Reactor Systems), Quebec City, QC, October 3-7 (2010).
6. Daub, K., Zhang, X., Noël, J.J. & Wren, J.C. J., "Influence of Temperature, Potential, pH and Gamma Irradiation on Carbon Steel Corrosion", Gordon Research Conference: Corrosion – Aqueous, Colby-Sawyer College, New London, NH, July 25-30, 2010, & Gordon Research Seminar, July 24-25 (2010).
7. M. Behazin, X. Zhang, J.J. Noël, and J.C. Wren, Comparative Study on Oxide Film Formation as a Function of Potential on Pure Co and Stellite, to be submitted to *Corrosion Science*.



## ACKNOWLEDGEMENTS

This research was funded under the Natural Science and Engineering Council of Canada (NSERC) and Atomic Energy of Canada Limited (AECL) Industrial Research Chair in Radiation Induced Processes. The <sup>60</sup>Co γ-irradiation cell and the electrochemical analysis equipment were purchased under a grant from the Canada Foundation for Innovation. The authors would also like to thank Dr. Todd Simpson of the University of Western Ontario Nanofabrication Facility for his assistance in cross-section analysis.

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