Ecole doctorale (préciser le numéro) :
ED 388 « Chimie Physique et Chimie Analytique de Paris Centre »

Titre du projet :
Toward a Sustainable Rechargeable Electrochromic Window for Smart Buildings

Structure d'accueil principale :
Laboratoire d'Electrochimie Moléculaire, Université de Paris, UMR CNRS 7591

Structure d'accueil secondaire :
National Research Council Canada - Nanotechnology Research Centre

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I. Description du projet de thèse – Research project

General context: Global warming and growing urban density are responsible for urban microclimates characterized by ever-increasing heat islands. For the comfort of residents and public health, cities must adapt while reducing their CO_2 emissions. Part of the solution will come from the construction of green buildings capable of dynamic adaptation and energy autonomy. A relevant strategy to increase the occupant comfort and energy efficiency of buildings is to use smart windows able to switch between transparent and opaque states upon application of a voltage.[1,2] Replacing the static low-emissivity windows in buildings by smart windows would result in an average of 10% energy saving, a gain that would help to reduce carbon emissions associated with the built environment.

Over the past four decades, the vast majority of research on smart windows were focused on electrochromic materials based on transition metal oxides or polymers.[1–3] However, only a few systems are commercially available so far due to durability, colour, switching speed, and cost issues.[4,5] Research efforts based on innovative approaches are therefore required to make these devices more effective and less costly. As a valuable alternative to the electrochromic materials, reversible electrodeposition of metals was recently proposed, offering stronger light attenuation with high contrast and excellent durability.[6,7] Another attractive prospect of smart windows, but still little explored, is their ability to store and release charges, exactly as a rechargeable battery does. Incorporating this functionality into the device would pave the way for the development of the next-generation of greener smart windows, capable of both retrieving the energy they consume and supplying energy to a building (see Figure 1 for the working principle of such green building).[8,9]

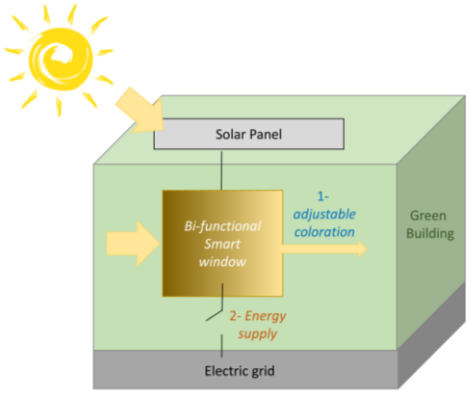

Figure 1. Working principle of a green building integrating second-generation smart windows.

Research Project: The main objective of the present research project is to establish the proof of concept of an innovative bi-functional smart window combining reversible electrochemical energy storage and electrochromism. While fully optically transparent in its discharged state, it will color upon application of a voltage, until turning entirely opaque once fully charged. Both coloration and charge storage will be fast and highly reversible, allowing the device to easily and rapidly recover full transparency upon delivering the stored energy.

The main originality of the smart window we propose here lies in the exploitation of metal and metal oxide electrodeposition/electrodissolution reactions (*i.e.*, conversion principle) that will be achieved at transparent electrodes in mild aqueous electrolytes. Using an appropriate metal/metal oxide couple as well as an electrolyte composition, it is possible to design a smart window with unprecedented features, outperforming all of those so far reported. We indeed expect to meet the following criteria:

(i) a high optical contrast and long-life cyclability, supported by the fact that a conversion-based mechanism is intrinsically less subject to degradation over long-term usage than standard electrochromic devices;

(ii) a stable operating voltage of 1.6 V, which coupled to an areal capacity as high as 2 $Ah \cdot m^{-2}$ (10-fold better than the state-of-the-art[9]) is expected to lead in an energy density of 3.2 $Wh \cdot m^{-2}$;

(iii) a sustainable device based on low-cost, abundant and non-toxic chemicals as well as non-flammable electrolyte, therefore better suited for large-scale mass production and societal acceptability.

Once the proof of concept will be established, the possibility of filing a patent will be considered with SATT IdF.

A second important objective of the present work will be to investigate the influence of the nanostructuring and modification of the underlying conductive electrode on the uniformity, efficiency and reversibility of the conversion processes, which is essential to achieve the expected performances. For the positive electrode, we will notably study conversion of semiconductive metal oxides at nanostructured (3D) transparent ITO electrodes (Figure 2), since our preliminary results already evidence a much better conversion efficiency and cyclability using such nanostructured conductive substrate. This part of the project will benefit of our long-term collaboration with Dr. K. Harris at NRC-Nano (secondary host structure) to produce highly-controlled and -reproducible nanostructured ITO films on glass substrates, with adjustable porosity and thickness (see part III for details).

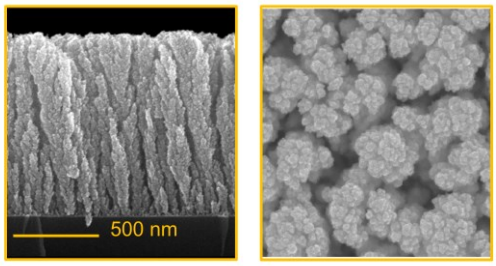

Figure 2. Side- and top-view SEM images of a 1-µm thick GLAD-ITO film.

These electrodes will be first assembled in a simple symmetric architecture I device (Figure 3), a configuration that was preliminary demonstrated by us as suitable for the reversible metal oxide electrodeposition at two face-to-face planar ITO electrodes. However, we will quickly move to architecture II where the metal will also have to be homogenously electrodeposited on a transparent conductive counter-electrode, which is desirable for large size windows due to an optimization of the electric field lines and ohmic drop. Specific efforts will therefore be made to obtain a uniform and reversible electrodeposition of metals on the surface of a transparent electrode.

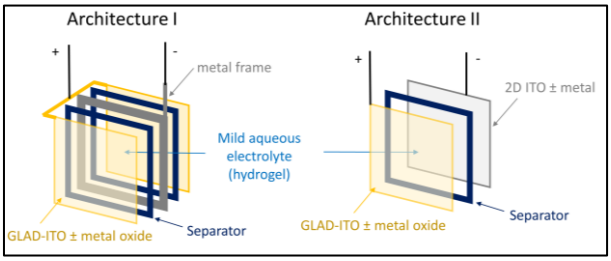

Figure 3. Architectures of the bi-functional smart windows.

Methodology, Time Frame (Oct 2020-Sept. 2023) and secondary host training

Task 1 - 8 months @ LEM: Quantitative UV/vis spectroelectrochemical analysis of the reversible metal oxide conversion reaction (dynamics of charge storage and coloration, cyclability) at standard GLAD-ITO electrodes (1-µm thick, porosity 50%) as a function of the aqueous electrolyte composition.
Deliverable 1: 10 cm^2 symmetric prototype I with optimized hydrogel electrolyte.

Task 2 - 8 months: Part I – 4 months @ NRC-Nano: Preparation of GLAD-ITO electrodes with adjusted porosity and thickness, preliminary investigation of their electrochemical/electrochromic properties, characterization of cycled GLAD-ITO electrodes by a range of spectroscopic methods (SEM, XPS, EDX…). **Part II – 4 months @ LEM:** Quantitative UV/vis spectroelectrochemical analysis of selected GLAD-ITO electrodes.
Deliverable 2: 10 cm^2 optimized prototype I with all metrics (areal capacity, optical contrast, response time, cyclability).

Task 3 - 8 months @ LEM: UV/vis spectroelectrochemical investigation of reversible metal electrodeposition at pre-functionalized planar ITO electrodes, SEM characterization of cycled electrodes.
Deliverable 3: 10 cm^2 prototype II with a suitable electrochromic negative electrode, and all metrics.

Task 4 - 6 months @ LEM: scale-up attempts based on architecture II. Large GLAD-ITO electrodes will be prepared at NRC-Nano by K. Harris.
Deliverable 4: 100 cm^2 prototype II.

Task 5 - 6 months @ LEM: Manuscript preparation (Deliverable July 2023) – PhD defence in Sept. 2023.

References

(1) Granqvist, C. G.; Arvizu, M. A.; Bayrak Pehlivan; Qu, H. Y.; Wen, R. T.; Niklasson, G. A. Electrochromic Materials and Devices for Energy Efficiency and Human Comfort in Buildings: A Critical Review. *Electrochim. Acta* **2018**, *259*, 1170–1182. https://doi.org/10.1016/j.electacta.2017.11.169.

(2) Yang, P.; Sun, P.; Mai, W. Electrochromic Energy Storage Devices. *Mater. Today* **2016**, *19* (7), 394–402. https://doi.org/10.1016/j.mattod.2015.11.007.

(3) Zhang, S.; Cao, S.; Zhang, T.; Fisher, A.; Lee, J. Y. Al_{3+} Intercalation/de-Intercalation-Enabled Dual-Band Electrochromic Smart Windows with a High Optical Modulation, Quick Response and Long Cycle Life. *Energy Environ. Sci.* **2018**, *11* (10), 2884–2892. https://doi.org/10.1039/c8ee01718b.

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(5) Stangel, L. South S.F. Startup Raises $65M for Its Smart Glass-Tinting Technology. *bizjournals*. 2017.

(6) Barile, C. J.; Slotcavage, D. J.; Hou, J.; Strand, M. T.; Hernandez, T. S.; McGehee, M. D. Dynamic Windows with Neutral Color, High Contrast, and Excellent Durability Using Reversible Metal Electrodeposition. *Joule* **2017**, *1* (1), 133–145. https://doi.org/10.1016/j.joule.2017.06.001.

(7) Islam, S. M.; Hernandez, T. S.; McGehee, M. D.; Barile, C. J. Hybrid Dynamic Windows Using Reversible Metal Electrodeposition and Ion Insertion. *Nat. Energy* **2019**, *4* (3), 223–229. https://doi.org/10.1038/s41560-019-0332-3.

(8) Li, H.; McRae, L.; Firby, C. J.; Elezzabi, A. Y. Rechargeable Aqueous Electrochromic Batteries Utilizing Ti-Substituted Tungsten Molybdenum Oxide Based Zn^{2+} Ion Intercalation Cathodes. *Adv. Mater.* **2019**, *31* (15), 1–9. https://doi.org/10.1002/adma.201807065.

(9) Li, H.; Firby, C. J.; Elezzabi, A. Y. Rechargeable Aqueous Hybrid Zn^{2+}/Al^{3+} Electrochromic Batteries. *Joule* **2019**, *3* (9), 2268–2278. https://doi.org/10.1016/j.joule.2019.06.021.

II. Description of the main supervision team

The Laboratoire d'Electrochimie Moléculaire (LEM) is a joined research laboratory between Université de Paris and CNRS (UMR 7591). It is internationally recognized in the field of molecular electrochemistry, especially for its contribution to the general understanding of all aspects of electron transfer chemistry coupled to both molecular changes and/or dynamical electron transport within molecules and biomolecules, but also within redox-active materials and catalytic films deposited on electrodes surfaces. The LEM is attached to the doctoral school ED388.

In this context, Dr. B. Limoges and Dr. V. Balland are currently developing a new research axis focusing on the electrochemical reactivity of mesoporous metal oxides in aqueous media, especially regarding their reversible charge storage properties. **This research is linked to the highly attractive and fast expanding field of rechargeable aqueous batteries**, which are considered as a viable and promising technology for large-scale electrochemical storage of renewal energies on account of their low-cost, eco-sustainability, and suitable energy densities**. In this highly competitive field, what distinguishes the research efforts carried out at LEM are rigorous fundamental studies that provide a better understanding of the charge storage mechanisms occurring at metal oxide films.** This takes full benefit of the strong expertise of both researchers in electroanalytical chemistry, and of a locally developed real-time UV-visible spectroelectroanalytical technique well suited to investigate (semi-)transparent thin-film electrodes. **It also relies on a long-term fruitful international collaboration with Dr. M. Brett (now retired) & Dr. K. Harris at NRC-Nano** (secondary host, with 9 common publications produced since 2011) for the preparation of highly controlled and reproducible mesoporous metal oxide thin films by GLAD (see part III for details).

B. Limoges and V. Balland recently obtained several significant results, by providing real fundamental insights into charge storage mechanisms occurring at TiO_2 and MnO_2 electrodes, highlighting notably the essential role of weak Brønsted acids and buffered media. These results (some still unpublished) are highly timely to clarify the reactivity of metal oxides in mild aqueous electrolytes, and challenge many of the mechanistic interpretations so far published in rechargeable aqueous batteries. It furthermore provides them the unique opportunity to develop innovative devices at the cutting edge of research, and notably the smart windows presented here, with a decisive advantage over the competition. **The recruited doctoral student will therefore be in a very stimulating environment where he/she will be able to acquire knowledge and skills that can be easily valorised on the job market, whether academic or industrial.**

Their research is currently receiving specific financial support from: DIM Respore (collaborative research network from Ile-de-France, PhD funding, 2019-21, PI V. Balland), ANR (AqReBat Project 2019-21 – PI B. Limoges) and CNRS (PICS funding, 2019-21, PI V. Balland).

Véronique Balland – Supervisor of the PhD student

Assistant professor, HDR, PEDR (since 2012), 44-years old, 38 articles total (including 15 as corresponding author), 1 patent, H-index = 21

Véronique Balland received her PhD degree in Bioinorganic Chemistry from University Paris Sud in 2002. In 2002–2004, she worked as research fellow at the Commissariat à l'Energie Atomique (CEA). In 2004, she joined the Laboratoire d'Electrochimie Moléculaire at the University Paris Diderot as an assistant professor. In addition to her teaching and research activities, she was heavily involved in the governance of the University Paris Diderot as member of the Conseil d'Administration (2009-18) and member of the presidential team in charge of financial affairs (2012-18).

At the LEM, she developed an original spectroelectroanalytical method to investigate the reactivity of transparent nanostructured metal-oxide (semi-)conductive electrodes (ITO, TiO_2, SnO_2…), eventually modified by functional (bio)molecules, for applications in catalysis, biosensing and more recently, reversible charge storage. Since 2006, she has been involved in 10 funded research projects, ranging from fundamental studies to pre-maturation/valorization aspects, and principal investigator of 6 of them (notably one ANR JCJC project).

She obtained her HDR in 2010, and officially supervised 4 PhD students since 2012 (including two foreign students and one ongoing PhD supervision). For the years 2019-2021, she benefits from a PICS grant from CNRS for international mobility to support her collaboration with Dr. K.D. Harris at NRC-Nano on the design of GLAD-electrodes for charge storage applications.

Benoît Limoges – Co-supervisor of the PhD student

DR CNRS, 54-years old, 92 articles total, 10 issued patents – 2 licensed, H-index = 33

Research Director at CNRS in the Laboratory of Molecular Electrochemistry since 2005. He was the director of the Laboratory of Molecular Electrochemistry (UMR CNRS 7591) from 2005 to 2016 and he currently heads a team of 3 Assistant Professors, 4 PhD students and 1 project engineer. He is co-author of 92 articles (H index = 33) and 10 issued patents including 2 licensed, and he has participated as coordinator or member in 28 funded research programs, including two ANR projects as coordinator. He has experience in technology transfer with the creation of the start-up company Easy Life Science to which he contributed, and he has been involved since 2009 in fundamental studies of electron transfer/charge transport in mesoporous semiconductive metal oxide electrodes (TiO_2, SnO_2, …) and in the development of spectroelectrochemical methods taking advantage of 3D nanostructured transparent metal-oxide electrodes (*e.g.*, ITO). This relatively recent research topic draws on his strong background in molecular and analytical electrochemistry, including his specific skills in modified electrodes, and on fruitful national and international collaborations with researchers in the field of materials, allowing for an original positioning in the scientific community. This project is also part of an evolution of his research topics toward the field of energy.

5 Most Relevant Publications of the team related to the present research project:

On electrochemical charge storage at metal oxide electrodes

1. *Accessing the two-electron charge storage capacity of MnO_2 in mild aqueous electrolytes.* M. Mateos, N. Makivic, Y-S. Kim, B. Limoges*, V. Balland* - submitted on Dec. 3rd 2019.
2. *On the Unsuspected Role of Multivalent Metal Ions on the Charge Storage of a Metal Oxide Electrode in Mild Aqueous Electrolytes.* Y-S Kim, K. D. Harris, B. Limoges,* V. Balland* (2019) *Chem. Sci.* **10**, 8752-63 – **part of the 2019 Chemical Science HOT Article Selection + Back cover illustration**
3. *Evidencing Fast, Massive and Reversible H^+ insertion in Nanostructured TiO_2 Electrodes at neutral pH. Where Do Protons Come From ?* Y-S Kim, S. Kriegel, K.D. Harris, C. Costentin, B. Limoges*, V. Balland* (2017) *J. Phys. Chem. C* **121**, 10325-35.

On metal oxide surface functionalization

4. Introducing Molecular Functionalities within High Surface Area Nanostructured ITO Electrodes through Diazonium Electrografting. Y-S Kim, S. Fournier, S. Lau-Truong, P. Decorse, C.H. Devillers, D. Lucas, K.D. Harris, B. Limoges*, V. Balland* (2018) *ChemElectroChem 5*, 1625-30
5. *Tuning the reactivity of nanostructured indium tin oxide electrodes toward chemisorption*. A. Forget, R.T. Tucker, M.J. Brett, B. Limoges*, V. Balland* (2015), *Chem. Commun. 51,* 6944-47

III. Description of the secondary host structure

Description of NRC-Nano:

The secondary training structure will be formally hosted at the National Research Council Canada – Nanotechnology Research Centre (NRC-Nano) which is located in Edmonton, Alberta, Canada on the campus of the University of Alberta. The National Research Council Canada (NRC) is Canada's foremost network of national laboratories and largest federal research and development organization. The NRC aligns with industrial and academic partners to conduct strategically significant and economically valuable research. The NRC is organized into 14 distinct research centres, each focussed on specific technologies or industrial sectors, and the Ph.D. student supported by the present project will be co-hosted at the Nanotechnology Research Centre (NRC-Nano), which is the most interdisciplinary and diverse research centre within the NRC. At NRC-Nano, the Ph.D. student will interact with chemists, physicists, medical scientists and engineers, and be exposed to a diversity of research environments including high performance analytical microscopy, cleanroom fabrication tools, bio-safety laboratories, and a wide range of additional characterization tools. Because industrial clients are integral to the NRC, the Ph.D. student will also have the opportunity to interact with researchers devoted to product development and industrial research. These are valuable "eye-opening" experiences, broadening the training environment and expanding the range of skills and background knowledge available to the student. Importantly, NRC-Nano is located on the campus of the University of Alberta (39000 students). As a result, NRC-Nano also enjoys links to numerous research labs, scientific tool sets and complementary networks of both scientific expertise and support services.

By partnering with NRC-Nano, two vital sets of specialized scientific infrastructure will be made available to the Ph.D. student. **First, the GLAD technique itself was pioneered in Edmonton, Alberta**[a] **and using the three complete GLAD systems that are in place, operational and available to the doctoral student, it will be possible to deposit a large assortment of specialized structures** (see Fig. 3 for a gallery of examples). The secondary supervisor (K. Harris) was personally involved during the early development of GLAD,[b] and he now has more than 20 years of experience depositing nanostructures in a wide assortment of materials and for a wide range of applications. The GLAD infrastructure/expertise currently available in Edmonton is among the best in the world, and the student will have access to this environment. Second, the microscopy-based materials science tools available at NRC-Nano are powerful and abundant: 4 scanning electron microscopes, 4 transmission electron microscopes, 2 atomic force microscopes, 2 focussed ion beam tools, and a suite of additional characterization tools are located at NRC-Nano and available for analysis of the student's electrochemical devices.

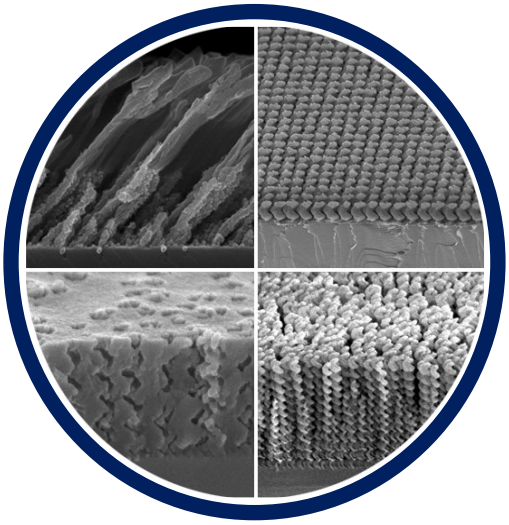

Fig. 3 – A selection of nanostructures formed by glancing angle deposition.

[a] *New materials at a glance*. M. Brett & M. Hawkeye (2008) *Science*, **319**, 1192-3;

[b] *A birefringent and transparent electrical conductor*, K.D. Harris, A.C. van Popta, J.C. Sit, D.J. Broer, M.J. Brett (2008) *Adv. Funct. Mater.*, **18**(15), 2147-2153; *Surface area characterization of obliquely deposited metal oxide nanostructured thin films*, K.M. Krause, M.T. Taschuk, K.D. Harris, D.A. Rider, N.G. Wakefield, J.C. Sit, J.M. Buriak, M. Thommes, M.J. Brett (2010) *Langmuir*, **26**(6), 4368-4376; *Indium tin oxide nanopillar electrodes inpolymer/fullerene solar cells*, D.A Rider, R.T Tucker, B.J. Worfolk, K.M. Krause, A. Lalany, M.J. Brett,J. M Buriak, K.D. Harris (2011) *Nanotechnology* **22**, 0858706

Dr. Ken Harris will personally oversee the Ph.D. student's training in the deposition of high surface area electrodes using the GLAD technique. GLAD electrodes will be prepared with different thicknesses (0.5-5.0 μm) and deposition angles (70-85°) to optimize the process, and subsequently, large-area electrodes up to 100 cm^2 will be prepared. Electrochemical deposition and characterization equipment is readily available at NRC-Nano, so the electrode structures can be modified by various MnO_2 electrodeposition processes (pre-developed at U. Paris) without incurring delays. Local experts in electrochemistry (primarily Dr. A. Jemere) and battery technology (M. Fleischauer) will assist in re-establishing these electrochemical processes within the secondary research structure. The extensive microscopy tools located at NRC-Nano will also be brought to bear: the GLAD ITO/MnO_2 structures will be characterized by SEM, TEM, x-ray photoelectron spectroscopy (XPS), energy dispersive x-ray spectroscopy (EDX) and electron energy loss spectroscopy (EELS), each of which is available at NRC-Nano. These tools will aid understanding of the failure mechanisms brought on by charge cycling, and they will allow us to devise adaptations to extend the cycle lifetimes. **Dr. Jae-Young Cho will personally assist the Ph.D. student's training in these analytical microscopy techniques.**

Kenneth D. Harris – Secondary PhD supervisor
Senior Research Officer, Nanomaterial Deposition and Characterization Team, NRC-Nano and Adjunct Professor, Department of Mechanical Engineering, University of Alberta
(B.Sc. in Engineering Physics, Ph.D. in Electrical Engineering, 42 years old, 59 articles total, 26 articles on glancing angle deposition, 24 articles on electronic devices, 1 issued patent, H index = 33)

Dr. Harris' expertise is distinct from and complementary to the research team at the Université de Paris. He is an expert in electronic devices and high surface area nanostructure deposition by glancing angle deposition (GLAD). He has extensive experience applying the GLAD technique to prepare high surface area nanostructures in a wide range of materials (including dielectrics, metals, semiconductors and organics). He has also used these GLAD-engineered nanofilms to build a range of functional electronic components including batteries and other electrochemical devices, as well as solar cells, biosensors, liquid crystal displays and molecular electronics.

Jae-Young Cho – main collaborator
Technical Officer, Developmental & Analytical Microscopy Team, NRC-Nano
(Ph.D. in Materials Engineering, 34 articles total, H index = 12)

Dr. Cho's expertise in nano-characterization using a range of microscopic/spectroscopic techniques, such as SEM, TEM, FIB, AFM and XRD, is also highly complementary. He has more than 20 years of experience in microscopic characterization, including failure analysis. His current work focuses on developing in-situ microscopic characterization methods for nanomaterials using in-solution AFM/SEM, high-temperature AFM/TEM, cryo-SEM/FIB/TEM and in-solution/high temperature XRD which will be critical research techniques for the success of this project.

National Research Council Canada | Conseil national de recherches Canada

NRC·CNRC

December 3rd, 2019

Re: **Expression of support for collaborative research program**

Dear Review Committee,

It is my pleasure to support the proposal by Dr. Balland to collaboratively train a Ph.D. student together with Dr. Ken Harris (Nanotechnology Research Centre, NRC-NANO). We are happy to host a portion of the Ph.D. student's studies at our facility in Edmonton, Canada, and to train the student in techniques such as nanostructure deposition and high performance microscopy.

The National Research Council Canada is in favor of expanding the strong relationship with Dr. Balland and colleagues. The team has previously used the glancing angle deposition technique developed in Edmonton to construct high-performance electrochemical devices. We would be delighted to have the opportunity to further explore this application area and gain new insights on charge storage and electrochromism in nanostructured electrodes. We currently have allotted $17,374/year in-kind support for collaborative work with Dr. Balland, including staff time and equipment use, of which the activities planned will be included.

NRC- NANO support for this grant application is based on the following:

1. There is tremendous potential for this team to make significant contributions towards the realization of high-surface area electrochemical devices.
2. Previous visits have been highly fruitful, leading to high impact publications.

We would be happy to host the Ph.D. student trained through this program at the Nanotechnology Research Centre, and through this, to reinforce the ongoing NRC- NANO /U.Paris collaboration. It is my distinct hope that this important research can continue to make an impact.

Sincerely,

Guillermo Ordorica-Garcia, Ph.D.
Director General, Nanotechnology Research Centre
National Research Council of Canada | Government of Canada
guillermo.ordorica-garcia@nrc-cnrc.gc.ca | Tel: 780-641-1610