



UMSAEP UM-UWC Interim Report

Visit to Columbia, Missouri, 01 March-31 May 2018

Molecularly imprinted Electrospun Polyamic acid as Electroactive transducers in sensor development.

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> UM-Columbia Host: Prof Sheila Grant Associate Dean of Research University of Missouri, College of Engineering

1. Overview

The research exchange visit to the University of Missouri (Columbia) represented the first steps towards a mutually beneficial research collaboration between the electrochemistry driven research focus of SensorLab (UWC) and the engineering expertise offered by the College of Engineering (Columbia, Missouri). SensorLab researchers introduced the polymer material extensively studied in their laboratories (UWC) as a suitable material for electrospinning. Preliminary testing and optimization of spinning conditions was done in South Africa, but the expertise and engineering focus of the Missouri team was required to produce high quality room temperature stable nanofibers of polyamic acid. Furthermore the technical expertise of Prof David Grant (Engineering) with respect to custom made electrospinning experiments delivered very high quality stand alone films of polyamic acid nanofibers. These nanofibers were further subjected to molecular imprinting of atrazine (test molecule) during the spinning step with great success.

2. Proposed Objectives (abbreviated)

The original objectives proposed for the 2018 visit (UWC to UM) were based on introduction of research focus areas and partners as well as exploring research areas of mutual interest, with short term outcomes in mind:

Objective 1: Introduction and orientation (week 1)

Orientation with respect to the laboratory, department and campus where the research visit will be hosted is necessary, since this is a first time exploration. Introductory lectures on the University of the Western Cape, Science faculty activities and in particular Chemistry department and the activities of Sensor Lab research group will be presented.

Expected outcomes:

Familiarization with the research context of both research partners and available research infrastructure, as well as a clearer perspective of the extent to which the respective research areas are mutually beneficial.

Objective 2: Electrochemical synthesis of a polymer based enzyme system (week 2-3)

Polyamic acid may be synthesized by two wet chemical routes using two different organic solvents. In both cases the polyamic acid synthesis delivers high yield (60%) and the FTIR characterization may be employed to verify the authenticity of the materials derived from chemical synthesis. The polyamic acid may be deposited at the working electrode interface as a semiconductive polymer thin film and characterized using microscopy, spectroscopy and electrochemistry. The in situ deposited polymer film will then be modified with the tyrosinase enzyme to produce the desired tyrosinase biosensor. *Expected outcomes:*

Teaching and training of polymer synthesis, electrodeposition and characterization to UM students. Subsequently a tyrosinase biosensors will be developed through immobilization of the enzyme at the electrodeposited polyamic acid interface, followed by its application to the detection of L-tyrosine The methodology to achieve this outcome will include small group tutorials on electrochemistry practice and quantitative analysis, laboratory demonstrations as well as the integration of analytical data obtained from microscopy and spectroscopy into the evaluation of the electrochemical performance of the sensor and biosensor. The quantitative analysis pertinent to sensor and biosensor systems will be highlighted.

Objective 3: Exploration of electrospinning of enzyme functionalized polyamic acid

(weeks 4-5)

An induction to the preparative routes employed by the Grant group for the development of nanostructured biocomposites will be done. A careful analysis of the properties of polyamic acid nanomaterials and their suitability for electrospinning strategies will be done, evaluating the effect of preparation voltage, time and distance, solvents used, collection methods etc. The recommended bioengineering method for the incorporation of the enzyme will be explored under the leadership of Prof Grant.

Expected outcomes:

The expectation is to produce a bioengineered tyrosinase functionalized polyamic acid nanocomposite using the electrospinning method or other suitable method at the discretion and under the direction of the research host. Should the materials synthesis be successful, the same quantitative analysis of the tyrosinase functionalized nanocomposite for the detection of L-tyrosine will be done. This work will have high merit for scientific publication in a suitable materials science journal.

3. Status of Proposed Objectives

Objective 1:

Prof Baker and Siyabulela Hamnca were both invited to give research presentations to Faculty members and research students. The first member of the SensorLab team to visit the labs of Prof Grant was Dr Fanelwa Ajayi (2016). She worked in Prof Grants lab to develop a nanoparticle modified electrochemical transducer for drug metabolism, with a view to address the challenge of efficient dose control in patients with HIV/Aids. Dr Ajayi introduced the interests of Prof Baker to Prof Grant and subsequent engagement (email) led to the realization of a research visit (Baker) and strong potential for future research collaboration.

Prof Baker and Siyabulela Hamnca (PhD student) traveled to Missouri on their introductory visit to the Missouri University (Colombia). Prof Baker spent two weeks on the ground exploring collaborations with faculty members in engineering and Chemistry and becoming acquainted with Mizzou campus life. At the time of the visit (March 2018) many students and staff members had unfortunately already travelled for holidays, but constructive engagement with faculty members was facilitated by the committed efforts of Prof Sheila Grant and Prof Wesley Bernskoetter. Prof Rod Uphoff and Ms Ashley Rhode was very helpful and accommodating in all of the logistical and travel arrnagements as well as setting up various appointments for meetings across faculties and departments.

Prof Baker and Siyabulela was invited to attend the weekly research group meetings of Prof Grant"s students and was introduced to the research scope (student presentations) and problem solving approach adopted by Prof Grant in a very constructive research management style. The practice of regular short term research progress meetings was also adopted by Prof Baker upon her return to SensorLab and has since delivered very constructive and efficient progress management, for her own students as well. Siyabulela Hamnca was invited to participate in the regular research meetings of the Grant group and also participated in research overview and regular research reporting presentations.

Very satisfactory accommodation was provided for Baker and Hamnca in the Excellence residence Hall. The rooms were spacious and well heated (necessary in the delayed snowfall experienced at the time) and the residence was fully equipped for short self catering support. Staff at the residence hall were all very friendly and helpful, making for a very pleasant stay indeed. Some facilities such as sports centre, ground transportation on student shuttles; was restricted from occasional use and required advance planning for access.

Objective 2:

Siyabulela Hamnca was able to successfully reproduce the synthesis of polyamic acid and do the necessary characterization by FTIR and cyclic voltammetry to confirm the integrity of the ynthesized polymer. Most of the other student in the Grant group at the time were already fully engaged in their own research activities and whilst none of them particularly needed to work in the area of polymer electrochemistry at the time of the visit, most of the learning and sharing took place as peer group learning in the group presentations. The students of the Grant group were very helpful and accommodating in facilitating the research activities of Mr Hamnca and the collaboration was a good networking experience, both in the lab as well as socially.

Objective 3:

Prof Dave Grant was key in fine tuning the electrospinning parameters of the custom made electrospinning facility in their research lab. The hands on approach and ability to tailor make the syste, to the requirements of polyamic acid spinning was both a luxury and a very novel experience for us. In South Africa we were only able to spin on commercial instruments which presented a number of restrictions, resulting in partial efficiency of spinning and materials with a high degree of beading. Great success was achieved with spinning high quality polyamic acid nanofibers and the characterization of the polymer nanofibers. Moreover, stable films of polyamic acid that could be peeled off the collector plate was prepared. Since polyamic acid is a polymer with very good semiconductor behavior (previous work from SensorLab) this was a very promising materials development which we would like to explore in future collaboration with respect to producing miniaturized paper based printed electrodes (future work). The ambition of introducing tyrosinase was not achieved during this visit since all agreed that working with enzymes directly in this early stage of materials synthesis would be both too costly and unpredictable due to the sensitivity of the enzymes to synthesis conditions. However the molecular imprinting of atrazine (veterinary biomarker) was attempted with measurable success and this approach was also of more direct interest to some of the other current research interests of the Grant group. Molecularly imprinted atrazine-polyamic acid was prepared reproducibly, but with very little time for full characterization.

Following the success of the initial (atrazine) imprinting of the electrospun fibres, the following research concept proposal was drafted by Prof Baker:



Figure 1: Conceptual diagram of immunosensor design based on electrospun polymer nanofibers

The proposal expanded on the in situ deposition of electrospun polyamic nanofibers (i) molecularly imprinted or (ii) surface functionalized with the an antigen of choice. The immunosensor thus produced may then be applied to a sample solution containing the TB antibodies and through the efficient transduction provided by the polymer interface the signal may be modelled as an impedimetric or amperrometric output. This is a common electroanalytical strategy adopted by Baker in her research with great success. However the orientation of the antigen on the transducer impacts directly on the availability of the antigen for binding to the antibody in solution and the efficiency of this type of sensor may vary greatly of the orientation of the antigen is not carefully controlled. It is in this respect that we believe the careful control of nanofiber synthesis (and even alignment) during electrospinning will add value to the integrity of the electvrodynamic interface during analytical application. These immunosensors may be designed with a variety of diseases in mind but for this project we had identified particular TB Ag/Ab detection strategy for SensorLab, which would be preceded by bovine TB Ag/Ab affinity sensors, developed with the Grant groups interests in mind. Prof Grant invited Prof Maria Fidelgo to participate in the collaboration, since the antibodies of interest to the UM researchers related to the detection of bovine TB is a particular focus area of Prof Fidalgo's research group.

We believe that the work proposed will have great potential for publication and conference presentations, cementing the UM-UWC linkage programme in a truly collaborative partnership focusing on scientific development, publication and human capacity development. However these were realistically identified as long term goals that would require a repeat visit (at least one more time) to finalise the output of the first visit in a scientifically validated manner. Unfortunately there were no UM students available to take over the research investigations from Siyabulela (due to the time of year) and we would like to motivate for a return visit by Siyabulela to continue working with Prof Dave and Sheila Grant on the Ag/Ab functionalized electrospun polyamic acid immunosensors.

4. Additional Noteworthy Activities

4.1 Scientific

Prof Baker was also invited onan extensive Chemistry department tour hosted by Prof Benschoetter. Prof Baker met with Prof Tim Glass (head of department, Chemistry) and elaborated on their mutual interest in electrochemistry research. Prof Baker also shared a presentation (PDF) with Prof Glass as a first line for information, should their be interest from colleagues in Chemistry department (UM) to collaborate with colleagues Chemistry (UWC). Proffs Baker and Glass also deliberated on the management system and leadership skills relevant to leading a successful academic and research proactive department. Prof Bernschoeeter (an Inorganic Chemist) also delighted in sharing the professional skills, equipment and infrastructural highlights of the UM Chemistry department. The departmental site visit was concluded with a campus walkabout and a visit to the University Faculty recreational facility; a truly memorable culinary experience.

4,2 Integration and Logistics:

Prof Baker and Mr Hamnca were accommodated on the main campus in Exccellence Hall and enjoyed a warm reception and hospitality throughout their stay. Ms Ashley took a personal interest in their well being and this was much appreciated in view of the difficult journey and travelling conditions due to inclement weather. The commitment to the people involved in the linkage programme as well as the greater ideological objectives of the linkage programme between UWC and UM was truly underscored by the care and friendly reception of all the staff at the International office (UWC) and Prof Rod Uphoff's team (UM). Siyabulela Hamnca was introduced to other students from UWC who were also on research exchange at the time of his visit and as a group they socialized with their Mizzou hosts and truly integrated into the college lifestyle. The Mizzou campus is user friendly, very efficient and very homely with a vibrant cultural atmosphere that makes it easy for visitors to get comfortable in a short space of time and really settle into enjoy Mizzou life. Ground transportation to the Columbia campus as well as in and around the town was efficient and easily accessible.

Acknowledgements:

We would like to take the opportunity to thank all the staff at the International relations office (UWC) as well as Prof Uphoff, Ms Ashley Rhode and all the colleagues at Mizzou for a warm and welcoming reception and very stimulating and productive research engagement. We want to specifically acknowledge the co-funding received from the International relations (UWC) c/o Prof Umesh Bawa. We also want to appreciate the constructive engagement with all Mizzou staff in Chemistry and Engineering, but particularly the commitment of Prof Sheila Grant, Prof Dave Grant, Prof Maria Fidelgo, Wesley Prof Bernskoetter and Prof Tim Glass.