University of Missouri South African Education Program (UMSAEP) Report 2025

Development of polyoxometalate decorated molecularly imprinted polymers for electrochemical sensing applications

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UNIVERSITY of the WESTERN CAPE

UMKC

SENSORLAB

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Introduction

Cancer is a preventable disease that affects people and animals. When cells undergo mitosis, there is a chance for abnormalities to arise. These abnormalities are taken care of by the immune system because it is considered an unknown species. However, this is not always the case. Most cervical cancers are caused by Human papillomavirus (HPV) and can be prevented by HPV vaccines. This vaccination is suggested by the World Health Organization (WHO) to be administered to young girls at age 9. Cancer treatment on the other hand is dependent on which stage of cancer is present in the body. Cancer treatment consists of surgery, immunotherapy, chemotherapy and radiotherapy. The treatment process can use one or more of these therapies and will be determined by a doctor.

Chemotherapy is a medication therapy where a patient receives a drug regimen for the specific cancer that they have. Monitoring of the patient during this treatment is crucial, as anti-cancer agents are strong molecules and contraindications should be looked out for. In the case of doxorubicin (DOX), there are several side effects that persist including: nausea, hair loss, sores on lips and in the mouth, diarrhoea and darkening of palms, soles and nails. Once the patient must stop the use of DOX, they need to monitor whether they have an irregular heartbeat, swelling of the lower legs and feet as well as shortness of breath. Cardiomyopathy is one of the most dangerous symptoms that DOX induces within patients and occurs at high concentrations of DOX. Therefore, the monitoring of levels of DOX in the body is extremely relevant to avoid the harsh side effects.

Research Outline

Initially, the proposed work of this study was to synthesize a POM and apply it in conjunction with a conducting polymer, to form a molecularly imprinted polymer (MIP) for doxorubicin electrochemical detection. The issue with this approach is that the conducting polymers will not be able to hold the shape of the cavity for long. There is also the question of doxorubicin's reactivity with the polymer and will the removal of it as a template be possible. To combat this, a dual monomer approach was taken where one part of the monomer can electropolymerize while the other part of the monomer is able to polymerize upon radiation, such as heat or UV light. A vinyl group is the perfect choice for this application and there are several functionalized

thiophene (Th) monomers commercially available. The monomer, 3-vinylthiophene (3-VTh), was chosen and purchased since there is Th available in the lab.

Due to the high cost of DOX, a model drug was used for the study i.e. prednisone which has a similar chemical structure and size compared to DOX as shown in **Figure 1**. The preliminary data obtained at the University of Missouri Kansas City (UMKC) will be the initial step to continuing the work at the University of the Western Cape (UWC).

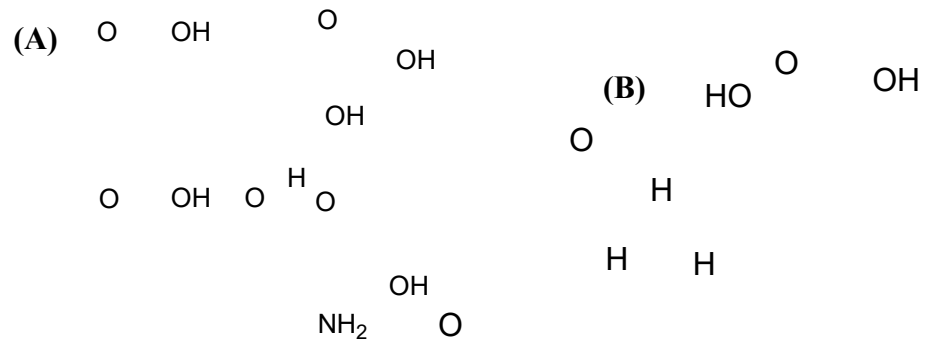

Figure 1: Structures of (A) doxorubicin and (B) prednisone

The vinyl functionalized thiophene will be exposed to thermal radiation and the vinyl group will polymerize around the prednisone to form the MIP on an ITO. The modified ITO is then submerged into a Th solution so that electropolymerization can take place and the film is conductive. Prednisone (the template) is removed from the polyvinylthiophene-ITO and the cavity that can interact specifically with the shape of prednisone is left behind. The electrochemical detection of prednisone will now be performed using the MIP-ITO.

Purpose of the POM in the sensor setup: There are a variety of POMs for many different applications. Typically, for catalytic oxidation reactions, phosphomolybdic or phosphotungstic acid is used. Phosphotungstic acid (PTA) is used as an acid catalyst while phosphomolybdic acid (PMA) is used in redox procedures. The issue is that Mo has 3 oxidation states that it moves between (6+/5+/4+) which questions its stability. PMA is often paired with carbon nanotubes or graphene as it passivates electrode surfaces. PMA is also known to have poor redox stability and have been improved on by doping with vanadium. The presence of vanadium aids to keep molybdenum at the 6+/5+ redox couple and increase its redox stability.

Aims and Objectives

The aim of this work is to fabricate a prednisone MIP onto an ITO to electrochemically detect prednisone in phosphate buffer. The objectives are as follows:

- Thermally polymerize the vinyl group of the 3-VTh monomer with PRD then,
- Electrochemically polymerize Th to crosslink it with (3-VTh and PRD) MIP-ITO
- Removal of PRD template from MIP
- Electrochemical detection of PRD in phosphate buffer

Research Activities

All electrochemical procedures were conducted using an EpsilonEC-2000 potentiostat. The electropolymerization of polythiophene was performed on an ITO (working electrode) with a platinum wire (Pt) counter electrode and a silver/silver chloride as the reference electrode. The preparation of the polythionine (PTh) film involved 0.1 M thiophene $NaClO_4$ in acetonitrile from 0 to 2 V at 100 mV/s. The electropolymerization of the functionalised monomer was attempted by placing a 0.5 mM of 3-vinylthiophene in $NaClO_4$ in acetonitrile and cycling using Cyclic Voltammetry (CV) from 0 to 2 V at 100 mV/s. Ultraviolet-Visible light spectroscopy (UV-Vis) was performed using a Hewlett Packard Diode Array Spectrophotometer (8452A) from 190 to 800 nm. UV-Vis was performed using bare and modified ITOs. The UV-Vis Thermal polymerization was conducted using a Gravity Convection Oven (DFA-7000) at 74,5 °C. The concentrations of PRD and 3-VTh were 0.5 mM and were used to perform ratio studies between them for the MIP fabrication.

The electropolymerization of PTh using Th and 3-VTh was carried out as shown in **Figure 2**. The polymerization of the PTh using Th was visible on the ITO as there was a brown colour present. For the 3-VTh, there was barely any colour change on the ITO but there was a dark powder depositing on the Pt counter electrode. Large amounts of noise was visible from the 3-VTh polymerization as shown in **Figure 2(B)**. In **Figure 2(A)**, the current peaks decrease in size from the first cycle to the tenth one.

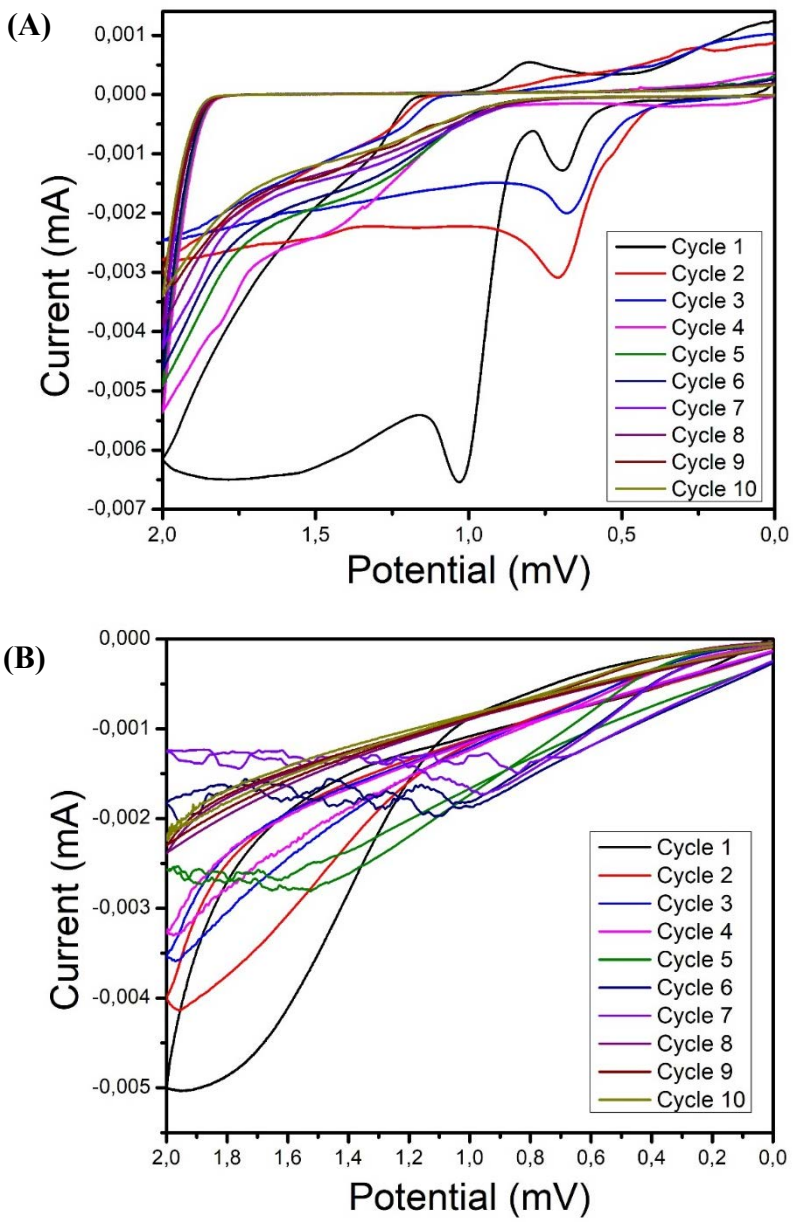

Figure 2: Electropolymerization of polythiophene using (A) thiophene and (B) 3-vinylthiophene from 0 to 2 V at 100 mV/s for 10 cycles.

The brown colour that is formed was then monitored using UV-Vis. A bare ITO was used as the blank. The first, second, third and tenth cycle were observed to determine if the polymer film is depositing onto the ITO with additonal cycles. The absorbance was shown to increase with the increase in cycles as shown in **Figure 3**.

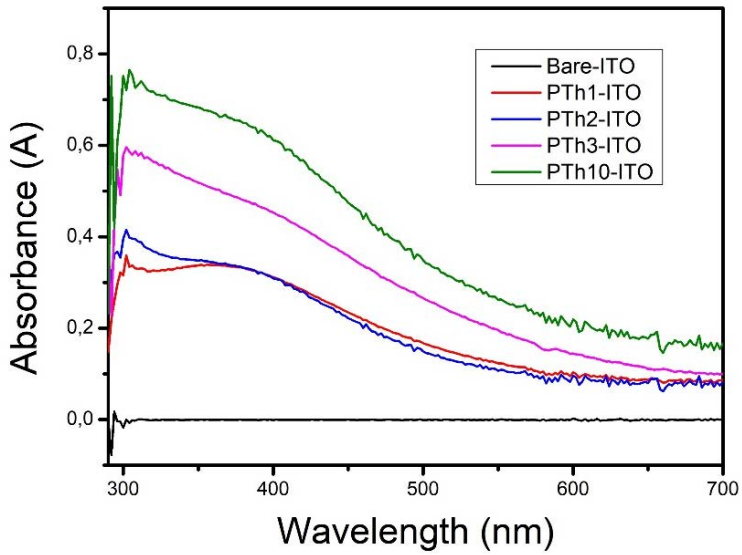

Figure 3: UV-Vis of the bare, first, second, third and tenth PTh polymerization cycle.

The thermal polymerization of the vinyl group of the 3-VTh monomer was conducted on ITOs by drop coating the monomer with an initiator. The initiator (hydrogen peroxide) assists to produce free radicals. In Figure 4 (A), the presence and absence of the initiator during the thermal polymerization was tested on a hotplate at 74,5 °C. This process was performed on a hotplate to instantly observe if the polymerization had taken place. The presence of the H_2O_2 was shown to assist with the thermal polymerization.

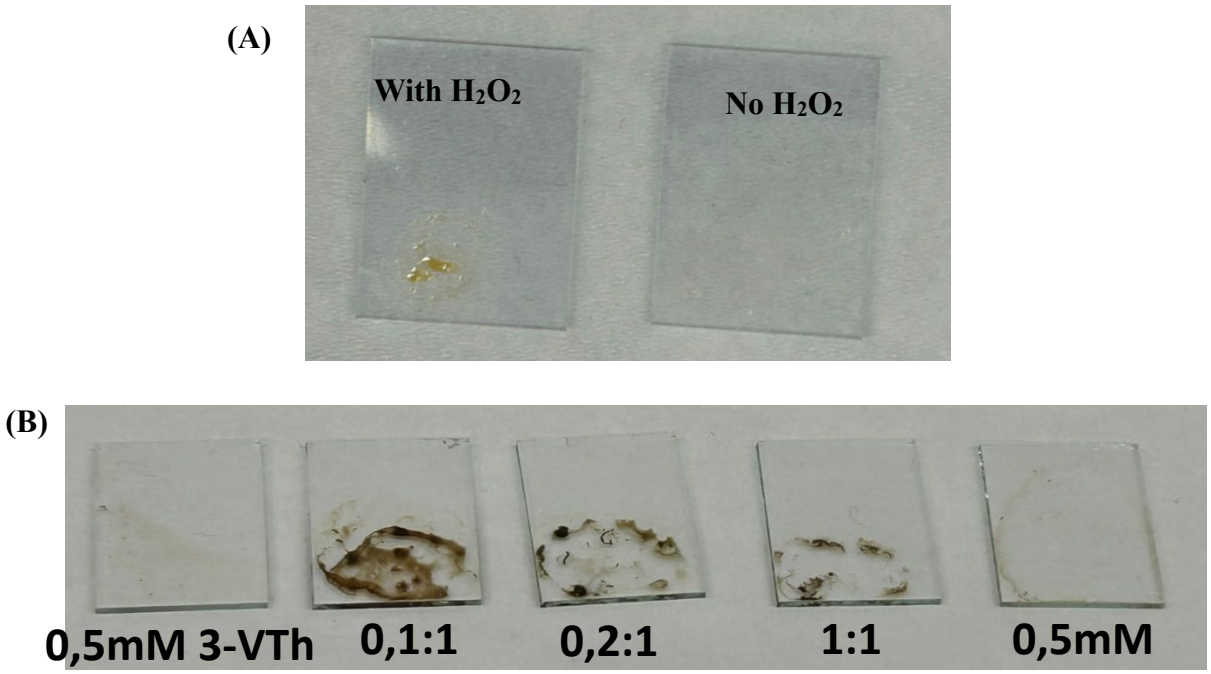

Figure 4: Thermal polymerization (A) with and without the H_2O_2 initiator and (B) Ratio study between PRD:3-VTh at 74,5 °C.

The next step was to prepare the MIP using different ratios of the monomer and template. The concentration of the PRD should not be too high and cause too many cavities to form in the polyvinyl. It becomes a concern if there is too little of the drug and few cavities form. Further characterization is therefore needed to confirm the MIP fabrication and compare the ratio performance. The polyvinyl is also soluble in acetonitrile and will not be able to remain as a film in the electropolymerization solution.

Conclusion and Future Work

The electropolymerization of polythiophene was achieved and the film was visible on the ITO. UV-Vis results display an increase in absorbance as the cycles are applied in CV, which confirms that the polythiophene film is depositing despite the decrease in current. This phenomena will need to be further investigated. Thermal polymerization of the vinyl group was observed but still requires confirmation of the MIP formation with further characterization. Validation that the thermal polymerization encases the drug as well as the template removal must still be conducted at UWC. The solvent choice needs to account for the vinyl group and prednisone solubility for proper separation of the two. The introduction to Molecular Docking procedure will be very useful for our research group because of the monomer and drug interactions that can be accounted for.

Additional Activities reported by Ashiqa Fakier-Lesch

I attended the weekly research group meetings for work discussions where Prof. Peng assisted with suggestions and constructive criticisms. Dr. Yong Li was so kind as to provide guidance on POM synthesis procedures for future POM-related work and was always ready to assist me in the lab. Syfur Tushar gave good insight on the POM characterization using XRD, SEM and EDS with the guidance of Dr. James Murowchick as well as introducing Differential Scanning Calorimetry (DSC). Anowar Hosen walked me through their NMR procedure and gave a good introduction on Molecular Docking. Nafisa Tasnim provided an introduction of the solar cell IV station where they test the efficiency and other parameters of their devices. I was present for the audit for chemical inspection which was a good learning experience. I attended the Community of Scholars Research Conference 2025 in Pierson Hall, where they had an

interesting talk on the use of AI in research and how fascinating the posters were on the use of computational applications.

I was able to go to Crown Centre mall, Wall Mart at the Shops at Boardwalk, Michaels in Zona Rosa, Joann, Ross and Plaza. I had the pleasure of attending the International Student Fellowship (ISF) gathering where many international students eat good food and play fun games. I happily attended the research group lunch at Aahaa in Overland Park. Afterwards, I was shown the Overland Park Arboretum and Botanical Gardens. I tried Iran chai milk tea at Desi Bites and then explored KC India Mart and Pan-Asia. I took a Sunday stroll to the WWI Memorial Museum. I was invited to a lunch picnic at Shawney Mission Park by the Pharmacy students where we tried various kind of foods. For Easter Sunday dinner, I was invited to a barbecue in Brookside. Nafisa, Syfur, Anowar and Atikur showed me around the Miniature Toy Museum. I witnessed the sweetest Bring Your Kids to Work Day on Volker campus. We had our final research group lunch at Pizza51 on campus. I saw some of the lovely art pieces at the Nelson-Atkins Museum of Art and the beautiful flowers in the Kauffman Legacy Park. I hope to ice skate at the Crown Centre Ice Terrace someday. I was accompanied by Syfur and Nafisa for a walk around the River Park.

Figure 5: Research group photo at introduction lunch (From left to right: Atikur Rahman, Anowar Hosen, Syfur Tushar, Prof. Zhonghua Josh Peng, Ashiqa Fakier-Lesch, Nafisa Tasnim).

Acknowledgements of Ashiqa Fakier-Lesch

The greatest appreciation to the University of Missouri South African Education Program (UMSAEP) for allowing and funding this learning opportunity. My gratitude goes to my supervisors Dr. Candice Cupido and Dr. Keagan Pokpas for their continuous support and guidance. Thank you to the National Research Foundation (NRF), South Africa for financially contributing to this project.

I am so grateful to be placed under the guidance of Prof. Zhonghua Josh Peng, I have learnt that research is much more interesting that I had originally thought. My appreciation extends to Dr. Yong Li for his synthesis advice and overall help, Anowar Hosen for the introduction to Molecular Docking software which will be very useful for the UWC Chemistry research group, Syfur Tushar for the DSC introduction and POM characterization advice, Nafisa Tasnim for the IV Station introduction and Atikur Rahman for the discussions on research applications. I appreciated everyone's willingness to help and listen even if it was not their specialty.

A big thank you to my dear neighbours Michael and Priscilla Ansong for always finding ways to include me on outings and dinners. May many blessings come to you and your family! Thank you so much to Diane Magers and Eric Storey for being so helpful and sweet during my stay in the Dimond Apartments at Diastole Centre. Kansas City is a beautiful place and I am so glad that I had the opportunity to experience it. I hope to visit again in the future!

Supervisor Summary

Having an international laboratory experience as a PhD student is extremely important and eye opening for the individual. This was a major take home from Ashiqa's visit to the US. Upon her return, Ashiqa was a different person, more experienced, mature and independent as a researcher. She experienced working in an international laboratory for the first time. Prof Peng was a very gracious host, despite his busy schedule he accommodated Ashiqa well. Ashiqa's knowledge of MIP systems has grown tremendously and she will apply this very valuable information in her PhD project moving forward. We look forward to growing the collaboration with Prof Peng in the future.