UMSAEP UM-UWC Student Exchange: Project Report

"Physio- and Electro-chemical Properties of Light-Driven Bimetallic Silver Coated Gold Nanostars"

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Abstract:

Metallic nanostructured materials, of which gold nanoparticles are the most popular, have shown great promise in a wide range of applications from medical to sensing. More recently, gold nanostars, the branched colloidal gold nano-systems composed of a core and several sharp branches have garnered tremendous interest in imaging, photothermal therapy, drug delivery, catalysis and sensing owing to their biocompatibility, optical properties, high surface area, and electronic capabilities. Current research is focused on developing green and environmentally friendly synthetic routes for materials preparation. Recently, light-mediated synthesis has been shown as an attractive means to reduce the reliance on harsh chemicals producing toxic by-products and high energy demands. The application of light during synthesis reduces the activation energy required for the reduction of metal salts to form nano-dimensional features. The proposed study is aimed at investigating the light-mediated synthesis of silver-coated gold nanostars as an environmentally friendly alternative to existing chemical synthetic routes. Herein, a seedless light-assisted, chemical synthesis of bimetallic silver-coated gold nanostars was investigated as a green synthetic route. A systematic investigation of reaction conditions (time, concentration, pH, temperature, exposure time, and intensity) and the effect of the shape, size, and material configuration on the physio- and electrochemical properties thereof are studied. Structural and morphological characterization of the prepared bimetallic nanostars by spectroscopic (SAXS, XRD, FTIR, Raman), microscopic (HR-SEM, HR-TEM, AFM), and electrochemical (CV, DPV, SWV, EIS) characterization techniques is proposed. The prepared bimetallic NS are investigated as possible electrode modifiers in electrochemical sensing applications.

The research study is guided by the following research questions:

- To what extent will a light-driven (UV and Visible) synthetic approach alter the structure and morphology of nanostructured materials during the silver coating of gold nanostars?
- How do reaction conditions, light source (wavelength), emission intensity, and exposure time affect the biocompatibility, stability, and physicochemical and electrochemical properties of the as-synthesized NMs?
- What mechanism would the green light-mediated synthetic route propose?
- Would a bimetallic nanostar offer improved active surface area and electron-transfer kinetics in electrochemical sensing applications?

Keywords: bimetallic gold-silver nanostars, light-driven synthesis, UV/Visible light, green chemistry

Background:

The research collaboration between Dr. Keagan Pokpas and Prof. Gary Baker started in May 2016 when Dr. Pokpas, then a Ph.D. candidate, travelled to The University of Missouri, Columbia campus as part of a 4-month research visit. The fully-funded collaborative research visit, afforded through the UMSAEP UM-UWC program focussed on two novel research projects cantered around nanomaterials preparation. During his stay, Keagan worked on (i) the electrochemical characterization of cyclic oxocarbons for application in the room temperature synthesis of metallic nanoparticles and (ii) their application in ionic liquid, gold nanoparticle decorated microfluidic paper-based electroanalytical devices (IL-AuNP-µPEDs) for environmental pollutant detection. Upon his return to South Africa, Dr. Pokpas completed the work which forms part of his Ph.D. dissertation. The findings resulted in two academic outputs, namely, (i) a peer-reviewed journal publication published in the Journal of Physical Chemistry (2018) and (ii) a poster presentation at the 72nd annual International Society of Electrochemistry (ISE) conference (full details below). The research visit offered Dr. Pokpas a wealth of knowledge related to nanomaterials preparation and characterization as well as microfluidic device design and machining. He further offered advice to the Baker group regarding electrochemistry. Since then, Dr. Pokpas has accepted a teaching position at UWC where he established a laboratory dedicated to paper-based microfluidic applications in electrochemical sensing and biosensing. Moreover, he incorporates the nanomaterials synthetic knowledge gained through his stay into his research and teaching of introductory and advanced Nanochemistry.

- N.E. Larm, J.B. Essner, K. Pokpas, J.A. Canon, N. Jahed, E.I. Iwuoha, G.A. Baker, Room-Temperature Turkevich Method: Formation of Gold Nanoparticles at the Speed of Mixing Using Cyclic Oxocarbon Reducing Agents, J. Phys. Chem. C. 122 (2018). doi:10.1021/acs.jpcc.7b10536.
- K. Pokpas, N. Larm, G. Baker, E. Iwuoha, N. Jahed, Electroanalytical, stripping voltammetric determination of metal ions at Room-temperature Gold Nanoparticle, Ionic liquid enhanced Microfluidic Paper-based Electroanalytical Devices (µPEDs), August 2021, 72nd Annual Meeting of the International Society of Electrochemistry (ISE). – Pre-recorded.

Current Project:

Nanostructured materials offer a great possibility for application in electrochemical sensors by increasing the active surface area of electrode materials, increasing the electron transfer kinetics

associated with redox activity, lowering the charge-transfer resistance, and enhancing the sensitivity and selectivity of the developed device. Owing to the toxic chemicals, elevated temperatures, and high energy demand associated with their synthesis, green methods for metallic nanoparticle preparation have been investigated. Harnessing the expertise of Prof. Gary Baker in the field of green nanochemistry, the current research project is aimed at the development of Au/Ag Nanostars following a light-mediated synthesis route. The study builds on the collaborative work established between the Baker Group and SensorLab, UWC over the 5-year period.

Ms. Ricaarda McDonald, a Ph.D. candidate in Chemistry at the University of the Western Cape, travelled to the University of Missouri-Columbia from the 1st of February – the 28th of April 2022 for a 3-month research visit. She was housed in the Baker Research Group where she had access to all chemicals, laboratory consumables, and research instrumentation required for the study.

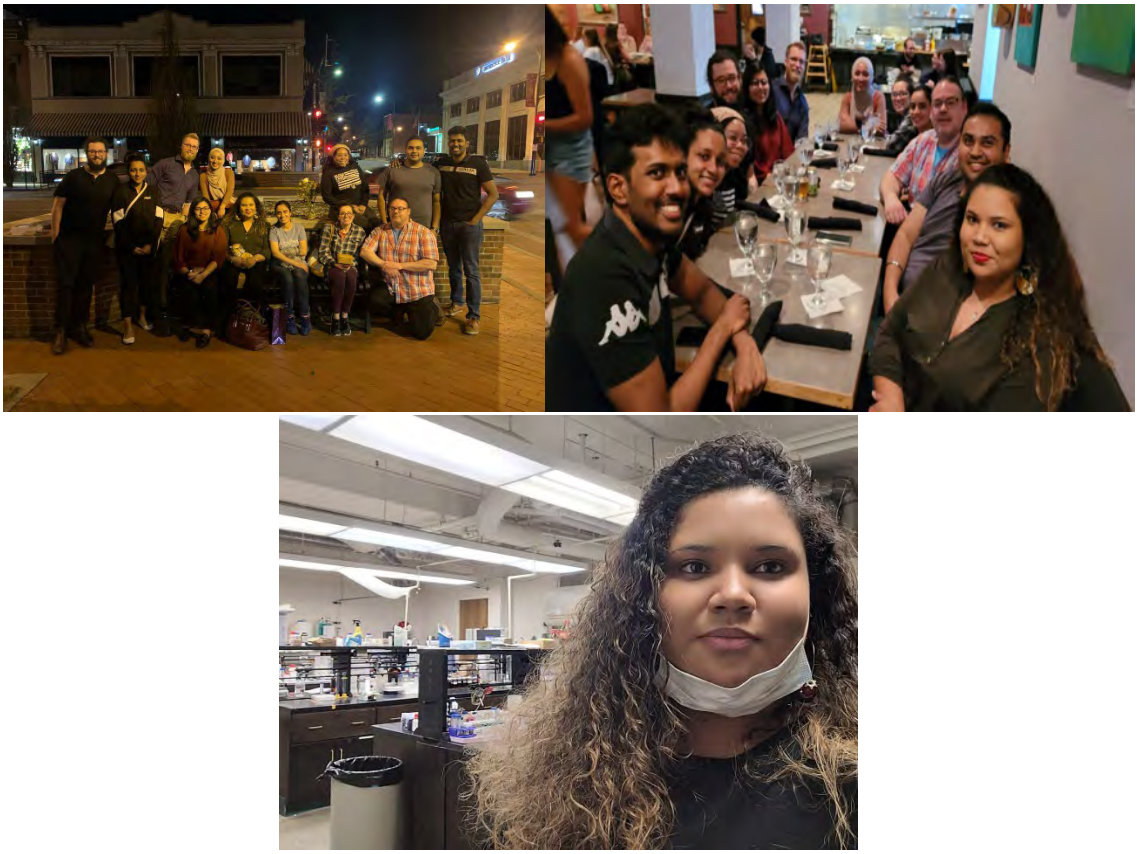

Figure 1: (a) Images of Ricaarda with the Baker research group and (b) in the laboratory at the University of Missouri-Columbia, Chemistry.

Under the supervision of Prof. Gary Baker and UM Ph.D. candidate, Asher Segal, Ms. McDonald received extensive hands-on training related to nanomaterials preparation and spectroscopic and microscopic characterization techniques. Initially, Ricaarda developed a comparative study on the effect of various reducing agents on the size and morphology of gold and silver nanoparticles. Thereafter, a light-mediated synthesis approach was investigated for the synthesis of bimetallic $Au_{(core)}$-$Ag_{(shell)}$ NPs**.** A variety of synthesis parameters, such as seed volume/concentration, reaction temperature, UV-emission wavelengths as well as UV-exposure times were investigated. The developed method was then applied to gold and bimetallic $Au_{(core)}$-$Ag_{(shell)}$ nanostars preparation and compared to chemical synthetic routes. Among others, the influence of reagent concentrations and

ratios, light sources, and exposure times on the physiochemical, structural, and electrochemical properties of the nanostars was investigated. Significant progress and training were conducted during the 3-month research visit. During her visit to UM, Ricaarda worked extensively on UV-Visible spectroscopy to study the influence of reaction parameters on the structure of the developed nanomaterials. This provided her with an in-depth understanding of the technique. The results were further confirmed by high-resolution transmission electron microscopy (HRTEM). Initial electrochemical studies were investigated along with Mr. Segal. The study was repeated, and further investigation and characterization were completed upon her return to the University of the Western Cape (UWC). Ms. McDonald successfully developed a green, light-driven approach for the coating of gold nanostars with silver to prepare the $Au_{(core)}$-$Ag_{(shell)}$ nanostars. It was found that the silver coating of nanostars was highly influenced by emission light wavelength, exposure time, and silver concentration. Further characterization via UV-Vis, HR-SEM, HR-TEM, DLS, FTIR, CV, DPV, SWV, and EIS was conducted. Specifically, electrochemical characterization yielded interesting information related to the effect of morphology on the electrochemical properties of nanostructured materials.

The research study resulted in the following research outputs:

Conference Proceeding:

- R. McDonald, A. Siegel, G. Baker, E. Iwuoha, C. Franke, K. Pokpas, Physicochemical and Electrochemical properties of Light-Driven Ag-coated AuNSs, August 2022, 73rd Annual Meeting of the International Society of Electrochemistry (ISE). – Pre-recorded

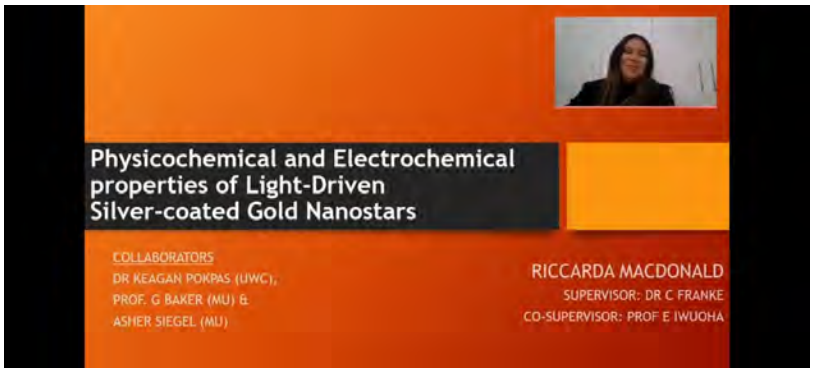

Figure 2: Ms. Ricaarda McDonald's pre-recorded oral presentation at the 2022 ISE annual conference.

Draft Manuscript:

- R. McDonald, A. Siegel, G. Baker, E. Iwuoha, C. Franke, K. Pokpas. Physicochemical and Electrochemical properties of Light-Driven Ag-coated AuNSs for publication in early 2023.

In addition to the research study, Ms. Ricaarda McDonald was exposed to a network of scientists from across the globe, made meaningful friendships, and met people from many cultures and backgrounds. The experience was fruitful and aided in developing Ms. McDonald as a well-rounded scientist. In addition to the work investigated under the proposed exchange, she gained a wealth of experience outside of the laboratory. Ricaarda ventured to the engineering faculty and received significant introductory training related to 3D printing and modeling during her stay which will assist her in her Ph.D. research.

Ongoing Work:

The three-month research stay proved to be a fruitful experience for Ms. McDonald and the collaboration between the two departments. The research study has since been completed upon her return to UWC and work is being done to complete outputs related to the work conducted. Revisions to the draft manuscript are currently being conducted by UWC and UM colleagues for possible publication in an international peer-reviewed journal publication. Depending on the availability of equipment, further characterization by SAXS, XRD, and Raman analysis may be conducted. It is envisaged to have the manuscript be published by February 2023.

The LED setup required for light-driven synthesis was sourced and has been set up in SensorLab, UWC, and will be used for continued research. The light-mediated green synthetic approach offers a unique avenue for future research in nanomaterials preparation by Dr. Pokpas and Dr. Candice Franke in the coming years. A training workshop related to light-driven synthesis will be offered to UWC, Chemistry postgraduate students in early 2023.

Ms. McDonald is further building on her introductory 3D printing training acquired at UM and participating in a 3D printing training course.

The developed bimetallic nanostars are currently being investigated for application in the electrochemical immunosensing of SARS-Cov-2 by Mr. Branham Kock (MSc student, UWC) and will further be applied in SARS-Cov-2 drug monitoring by Ms. McDonald in 2023.

Budget:

The UMSAEP UM-UWC funding was utilized to cover the costs of Ms. Ricaarda McDonald's research exchange to UM in 2022. The funds were supplemented by the SA National Research Foundation (NRF) through Dr. Pokpas and Dr. Franke. Prof. Baker provided running costs for materials and consumables in his laboratory.

Acknowledgments:

On behalf of Dr. Keagan Pokpas, Ms. Ricaarda McDonald, and all researchers involved in the study, we would like to express our sincere gratitude to the UMSAEP UM-UWC student exchange programme and Prof. Rodney Uphoff and Prof. Gary Baker for the opportunity. The student exchange provided a unique and meaningful opportunity to extend the collaboration between Prof. Baker and Dr. Pokpas and conduct an interesting and unique study on light-assisted synthesis which will be a useful research area to include at UWC. Among others, a useful networking opportunity and a wealth of knowledge were gained in the field of green nanochemistry. The student exchange afforded to Ms. McDonald demonstrated a vital avenue for her development and she is extremely thankful for the unique opportunity.