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IDRC GRANT / SUBVENTION DU CRDI : - CANADA-SOUTH AFRICA TRILATERAL RESEARCH CHAIR IN NANOMATERIALS FOR CLEAN WATER

Trilateral Research Chairs Initiative – Final Report

Project Title: Light-Matter Interactions: Development of "smart" Photoactive Materials for Environmental Applications

Project Number: 108569-001

Research Chairs:

Canada: Prof. Juan Scaiano, University of Ottawa

South Africa: Prof. Tebello Nyokong, Rhodes University

Kenya: Dr. Edith Amuhaya, United States International University – Africa

Project Duration: 07/2017 to 01/2023

Project Abstract

This project set out to use light to solve environmental issues that are of high importance in Africa and beyond. In addition, the project chairs regarded high quality personnel training as a major component of the research, as the generation of skilled scientists with the knowledge, abilities and international network to solve long-term problems. Combined, the three research groups utilized their extensive experience in the use of light to trigger photophysical or photochemical processes, which capitalize on their complementary skills in synthesis, nanotechnology and application of photochemistry to health, such as therapeutics or diagnosis, as well as to environmental issues. Following the growing interest in combining nanomaterials with photosensitizers for photodynamic antimicrobial chemotherapy (PACT) and photodegradation of pollutants in water sanitation, the aim of the project, therefore, was to link metallic and/or metal oxide nano/micro-particles to materials that could enhance their environmental performance, for example by decorating them with metal nanostructures, or with porphyrin-type complexes such as metallophthalocyanines and metalloporphyrins to create new hybrid materials for their intelligent use in environmental control. For this, new materials were synthesized and characterized, and their applications on PACT, degradation of pollutants as well as photo-sterilization of potable water are being explored.

Keywords: photochemical, photodynamic antimicrobial chemotherapy, photodegradation, pollutants, water sanitation, porphyrin-type complexes, photocatalysis, nano/micro particles.

Project Rationale:

Despite various mitigation efforts, the South African and Kenyan governments are struggling to meet their countries' demand of quality water for domestic and industrial purposes. This is attributed in part to variable rainfall patterns, pollution from industrial effluents and municipal pollution brought about by informal settlements near rivers.

The project therefore focused on the use of nanotechnology to develop materials that could provide solutions for water and soil decontamination as well as design new systems to reduce the cost of the actual methods of purification. Through incorporation of metal oxides from metals such as Titanium, and Niobium, which are naturally available in South Africa and Canada, the project aimed to improve the activity of the materials in pollutant photodegradation and PACT through photocatalytic reactions.

An agreement between Luzchem Research, Inc., and the Canadian group set out to develop a solar operated flow water purification system aimed at purification of drinking water. The ultimate goal was to develop an innovation that would not only lead to increased access to quality water for improved health, but would also lead to a reduction in the costs of purifying the water by municipalities.

Project Objectives:

The objectives for the project were:

1. Synthesis of asymmetric porphyrin-type complexes
2. Fabrication and functionalization of nano/micro-particles with organic, metallic, or oxide modification
3. Coordination of porphyrin-type complexes to nano/micro-particles (see above proposed mask disinfection strategy)
4. Study of the photophysical behavior of porphyrin-type complexes and their conjugates with nanomaterials
5. Study of the PACT activities of the conjugates
6. The use of the conjugates for the degradation of organic pollutants
7. The use of functional nanoparticles to photo-sterilize potable water using solar photocatalysis in flow systems.
8. Study the biocompatibility and potential toxicity of the new materials and their potential use in the field.

Methodology

Porphyrin complexes were synthesized using either Adler or Lindsey protocol depending on the reagents used in the synthesis. Purification process included solvent extractions, and column chromatography. For column chromatography, silica gel was used and different solvent systems employed depending on the properties of the target porphyrins. Multiple separations were carried out to ensure compound purity. Metal insertion was also carried out using known protocols, using the corresponding metal salts. Purification of the metallated porphyrins was achieved using column chromatography.

Characterization of these metallated porphyrins was carried out using ^{1}H NMR, ^{13}C NMR, FTIR, Mass spectrometry as well as elemental analysis. The photophysical studies were carried on all synthesized porphyrins. These included UV-Visible spectroscopy, fluorescence studies, quantum yield studies, and singlet oxygen generation.

Synthesis of nanoparticles was carried out using literature protocols, either by electrospinning and rotary jet- spinning. Materials characterization was carried out through Electronic microscopy (TEM, SEM), diffuse reflectance, solid-state fluorescence and X-ray photon spectroscopies. Amount of metal added was determined by inductively coupled plasma (ICP-OES). The synthesized nanoparticles contained capping agents which allowed for the coordination of porphyrin-type complexes. The nanoconjugates were then used for photodynamic antimicrobial chemotherapy (PACT) and photodegradation of pollutants.

The microbial studies involved use of methicillin-resistant *Staphylococcus aureus* (MRSA), carbapenem-resistant *Escherichia coli* (*E. coli*) and *Pseudomonas aureginosa* (*P. aureginosa*).

These studies utilized known protocols, with slight variations, depending on the bacteria being studied.

Flow systems as those that will be needed for water treatment were developed and scaled up to the 20-liter scale. Additionally, fully flow compatible black TiO_2 catalysts were developed and tested for organic degradation under flow and visible light illumination. To address the low mechanical strength of TiO_2 fibers, focus was placed on improving the macroscopic and mechanical properties of the semiconductor fibers. There were continued studies in the use of glass wool, activated by oxygen plasma, to deposit TiO_2 as well as the synthesis of TiO_2 on the surface of titanium metal foams. These experiments were designed to facilitate flow techniques and to employ low cost materials. This led to the development of new catalysts based on black TiO_2. These materials were tested on a series of dyes and pharmaceuticals.

Project Activities

Various activities were carried out throughout the five-year project duration. These included:

a) **Lab based activities**
   Lab experiments were carried out by all the three research groups in Kenya, South Africa and Canada. These were based on the three research groups' experience in the use of light to trigger photochemical or photophysical processes. Additionally, the groups capitalized on their complementary skills in the areas of nanotechnology, organic synthesis, mechanistic studies and photochemical studies to develop materials that were found to have potential use in large scale destruction of disease causing pathogens as well as industrial pollutants. The synthesized metal complexes were characterized and coordinated to nanoparticles and glass wool and their photophysical properties and photocatalytic properties experimentally determined. Finally, the materials developed were tested for their antimicrobial properties as well as their ability to deactivate industrial contaminants.
b) **Capacity Building**
   A major component of the project involved training of new students in the project research area. This saw the training of undergraduates, masters and PhD students across the three research groups. The project made a deliberate effort to recruit and train female students in a bid to bridge the gender gap.
c) **Student exchange program**
   The project made it possible for students to travel between the three research groups to learn new research skills. Additionally, through these visits, the students gained access to research equipment that was not available in their home research lab. This enabled them gain the much needed hands on skills required in their future careers. These visits were very successful during the first half of the project, but since March 2020 they were severely limited by the COVID pandemic. While the interaction among the three groups was continued throughout the project, much of the late research was performed locally by team members that would otherwise have participated in exchanges
d) **Conferences**
   The project facilitated the participation of both local (in respective countries) and international conferences in the three research groups. This especially allowed the students showcase their research work, while creating an opportunity for them to network.
e) **Workshops/Seminars**

As part of data dissemination, the three research groups organized and participated in various workshops and seminars. These also provided opportunities for the students to learn from the discussions.

f) Publications

The research outputs generated several publications in peer-reviewed journals and a few more are currently in preparation or under review.

The success of the project's activities highly depended on timely communication and co-ordination between the three research groups. The student exchange visits required consideration for each research group's preferences and schedules. Unfortunately, the COVID-19 pandemic interfered with these visits. However, to keep the learning going between the three groups, the three groups organized online seminars involving guest speakers. While the COVID-19 pandemic slowed down activities, it did not completely stop the project. The three research groups were able to find ways of keeping the project going, and students learning. For example, to maintain social distancing, research students were allowed to work in the lab in shifts. Also, while there were travel restrictions put in place globally, the Kenyan research group was able to send samples to the South African research group for analysis.

Project Outputs

Below is a breakdown of the project outputs for the project.

i) Publications

In total, 28 research articles, 1 book, 1 book chapter, 1 published paper from an international scientific congress were realized during the course of the project. These were?

a) Research Articles

1) Hainer, A. S.; Hodgins, J. S.; Sandre, V.; Vallieres, M.; Lanterna, A. E.; Scaiano, J. C., » Photocatalytic Hydrogen Generation Using Metal-Decorated TiO2: Sacrificial Donors vs. True Water Splitting » ACS Energy Lett. 2018, 3, 542-545.
2) Azole Sindelo, Nagao Kobayashi, Mutsumi Kimura and Tebello Nyokong Physicochemical and Photodynamic Antimicrobial Chemotherapy Activity of Morpholine-Substituted Phthalocyanines: Effect of Point of Substitution and Central Metal J. Photochem. Photobiol. A, 374 (2019) 58-67.
3) Mapukata S., Osifeko O.L, Nyokong T., Phthalocyanine-cobalt ferrite based nanocomposites as dual photocatalysts for photodegradation of methyl orange and photoreduction of chromium(VI) Heliyon 5 (2019) e01509. doi: 10.1016/j.heliyon.2019.e01509.
4) Mapukata S., Kobayashi N., Kimura M., Nyokong T., Asymmetrical and symmetrical zinc phthalocyanine-cobalt ferrite conjugates embedded in electrospun fibers for photocatalytic degradation of azo dyes: Methyl Orange and Orange G. J. Photochem. Photobiol. A: 379 (2019) 112-122.
5) Elhage, B. Wang, N. Marina, M.L. Marin, M.Cruz, A.E. Lanterna and J.C. Scaiano, "Glass wool: a novel support for heterogeneous catalysis", Chem. Sci., 9, 6844-6852 (2018).
6) J.C. Scaiano, The many faces of Titanium Dioxide: From H2 generation and water decontamination, to Green Catalysis Inspired by Crop Rotation

Practices in Agriculture, International Synthetic Photochemistry Forum, Plenary lecture, Wuhan, China, Nov. 2018.
7) R Soy, B Babu, D Oluwole, N Nwaji, J Oyim, E Amuhaya, E Prinsloo, J Mack and T Nyokong Photophysicochemical properties and photodynamic therapy activity of chloroindium(III) tetraarylporphyrins and their gold nanoparticle conjugates Journal of Porphyrins and Phthalocyanines (2019) 23, 34-45.
8) Babu B., Amuhaya E., Oluwole D., Prinsloo E., Mack J., Nyokong T., Preparation of NIR absorbing axial substituted tin(IV) porphyrins and their photocytotoxic properties MedChemComm (2019), 10(1), 41-48.
9) Mapukata S., Hainer A.S, Lanterna A.E, Scaiano J.C, Nyokong T., "Decorated titania fibers as photocatalysts for hydrogen generation and organic matter degradation", J. Photochem. Photobiol. A: Chem. 388, 112185 (2020).
10) Teixeira R. I., de Lucas N.C., Garden S.J., Lanterna A.E., Scaiano J.C., "Glass wool supported ruthenium complexes: versatile, recyclable heterogeneous photoredox catalysts", Catal. Sci. Technol.,10, 1273-1280 (2020).
11) Otieno, S., Lanterna A.E., Mack J., Derese S., Amuhaya E.K., Nyokong T., Scaiano J.C., “Solar Driven Photocatalytic Activity of Porphyrin Sensitized TiO2: Experimental and Computational Studies” Molecules, 26, 3131 (2021). https://doi.org/10.3390/molecules 26113131.
12) Mapukata S., Hainer A.S., Lanterna A. E., Scaiano J.C., Nyokong T., "Decorated titania fibers as photocatalysts for hydrogen generation and organic matter degradation", J. Photochem. Photobiol. A: Chem. 388, 112185 (2020).
13) Makola C.L., Nyokong T., Amuhaya E.K, Impact of axial ligation on photophysical and photodynamic antimicrobial properties of Indium (III) phenylmethylthio porphyrin complexes linked to silver-capped copper ferrite magnetic nanoparticles, Polyhedron, 193 (2021) 114882.
14) T. Nyokong, B. P. Ngoy, E. Amuhaya, Overcoming challenges facing African researchers, Nature Materials, (2021), 20(4), 570 – INVITED
15) Mapukata S., Britton J., Osifeko O.L, and Nyokong T., The improved antibacterial efficiency of a zinc phthalocyanine when embedded on silver nanoparticle modified silica nanofibers, Photodiagnosis and Photodynamic Therapy, 33 (2021) 102100.
16) Mapukata S., Sen P., Osifeko O.L., Nyokong T., The antibacterial and antifungal properties of neutral, octacationic, hexadecacationic Zn phthalocyanines when conjugated to silver nanoparticles, Photodiagnosis photodynamic Therapy 35 (2021) 102361.
17) Gawargy T.A., Costa P., Lanterna A.E., Scaiano J.C., “Photochemical benzylic radical arylation promoted by supported Pd nanostructures”, Org. Biomol. Chem., 18, 6047-6052 (2020).
18) Gómez M.J., Benavente-Llorente V., Hainer A., Lacconi G.I., Scaiano J.C., Franceschini E.A., Lanterna A.E., "Evaluation of different Ni–semiconductor composites as electrodes for enhanced hydrogen evolution reaction", Sustainable Energy & Fuels, 4, 3963-3970 (2020).

19) Lemir I.D., Argüello J.E., Lanterna A.E., Scaiano J.C., “Heterogeneous photocatalysis of azides: extending nitrene photochemistry to longer wavelengths, Chem. Comm. 56 (70), 10239-10242 (2020).
20) Wang B., Lanterna A. E., Scaiano J.C., “Mechanistic Insights on the Semihydrogenation of Alkynes over Different Nanostructured Photocatalysts”, ACS Catal. 11 (7), 4230–4238 (2021).
21) Otieno S., Lanterna A.E., Mack J., Derese S., Amuhaya E.K., Nyokong T., Scaiano J.C., “Solar Driven Photocatalytic Activity of Porphyrin Sensitized TiO2: Experimental and Computational Studies” Molecules, 26, 3131 (2021). https://doi.org/10.3390/molecules 26113131.
22) Fournier K., Marina N., Joshi N., Berthiaume V.R., Currie S., Lanterna A.E., Scaiano J.C., "Scale-up of a photochemical flow reactor for the production of lignin-coated titanium dioxide as a sunscreen ingredient", J Photochem. Photobiol., 7, 100040 (2021).
23) Mejía-Giraldo J. C., Scaiano J.C., Gallardo-Cabrera C., Puertas-Mejía M.A., “Photoprotection and Photostability of a New Lignin-Gelatin-Baccharis antioquensis-Based Hybrid Biomaterial”. Antioxidants 10 (12), 1904 (2021).
24) Cely-Pinto M., Scaiano J.C., “Photoenolization as a convenient driver for the synthesis of plasmonic nanostructures”, Photochem.Photobiol. Sci., 20 (12), 1611-1619 (2021).
25) Gawargy T.A., Wang B., Scaiano J.C., “Unveiling the Mechanism for the Photochemistry and Photodegradation of Vanillin”, Photochem. Photobiol. , 2021 DOI: https://doi.org/10.1111/php.13520.
26) Yaghmaei M., Villanueva M., Martín-Garcia I., Alonso F., Zhang X., Joshi N., “Photosensitized selective semi-oxidation of tetrahydroisoquinoline: a singlet oxygen path”, Photochem. Photobiol. Sci., 1-7 (2022).
27) Sindelo, Britton J., Lanterna A.E., Scaiano J.C., T. Nyokong, "Decoration of glass wool with zinc (II) phthalocyanine for the photocatalytic transformation of methyl orange", J. Photochem. Photobiol. A: Chem., 432, 114127.(2022).
28) Oyim J., Omolo C.A, Amuhaya E.K (2021) Photodynamic Antimicrobial Chemotherapy: Advancements in Porphyrin-Based Photosensitizer Development. Frontiers in Chemistry: Organic Chemistry. doi.org/10.3389/fchem.2021.635344.

b) Books and Book Chapters

1) BOOK: J.C. (Tito) Scaiano, Photochemistry Essentials; ACS In Focus Series, American Chemical Society, 2022. DOI: 10.1021/acsinfocus.7e5031
2) BOOK CHAPTER: Ram K. Gupta, Conducting Polymers, Eman Abdallah Ismail, Mbuso Faya, Edith Amuhaya, Calvin A. Omolo, Thirumala Govender, Biodegradable Polymers: Synthesis to Advanced Biomedical Applications, (2022). CRC Press, Boca Raton, ISMB: 9781003205418, https://doi.org/10.1201/9781003205418.

c) Published papers from International Scientific meetings/congresses

1) J. Scaiano*, A.E. Lanterna*. “A Green Road Map for Heterogeneous Photocatalysis” Pure Appl. Chem. 2019, Invited article. Published online: DOI: https://doi.org/10.1515/pac-2019-0207

ii) Conferences/Workshops/Seminars/Symposia

Throughout the project a total of 25 conference, 3 workshop and 6 symposia/seminar presentations were made. These were:

a) Conferences:

1) Amuhaya E. Development of Photoactive Materials for Water Decontamination using Photodynamic-antimicrobial Therapy. International Conference of the Natural Products Research Network for Eastern and Central Africa – Kenya (NAPRECA – K) 9th February 2018 at SAJOREC, JKUAT, Kenya.
2) Oloo S., Amuhaya E., Synthesis and Photo-Physical Studies of Structurally Modified Porphyrin Dyes for application in Water Treatment for Domestic Use. Best western Meridian Plus, Nairobi), May 22nd - 24th,2018.
3) Khisa J., Amuhaya E., Synthesis and Photophysical Properties of Porphyrin Based Compounds for Application in PACT for Water Treatment. Best western Meridian Plus, Nairobi), May 22nd -24th, 2018.
4) Oyim J., Ngoy P., Mack J., Nyokong T., Amuhaya E., Synthesis, photophysical studies and TD-DFT calculations of 5,10,15,20-tetrakis [4-(benzyloxy)phenyl] porphyrinato indium (III) chloride. Tenth international conference on porphyrins and Phthalocyanines, ICPP-10, Munich, Germany, July 1-6, 2018.
5) Nyokong T.,The role of nanostructured materials in enhancing the photophysical behaviour of phthalocyanines, Atlantic Basin Conference on Chemistry (ABCChem) – 24-26 January, 2018; Cancún, Mexico. INVITED.
6) Matlou G.G., Kobayashi N., Kimura M., Nyokong T., Physicochemical properties of metallophthalocyanines when conjugated to magnetic nanoparticles, Atlantic Basin Conference on Chemistry (ABCChem) – 24-26 January, 2018; Cancún, Mexico.
7) Mapukata S., Nyokong T., Phthalocyanine-cobalt ferrite based composites as bifunctional photocatalysts in water purification, Atlantic Basin Conference on Chemistry (ABCChem) – 24-26 January, 2018; Cancún, Mexico.
8) Mapukata S., Nyokong T., Laser induced photodegradation of orange g using phthalocyanine – cobalt ferrite magnetic nanoparticle conjugates electrospun in polystyrene nanofibers. Electrospin 2018 – an International conference, Wallenberg Research Centre at Stias, Stellnbosch, South Africa, 16th to 18th July, 2018.
9) Lebechi A.K., Nyokong T., Mack J., Laser induced photocatalytic degradation of orange g using halogenated bodipy dyes embeded in polystyrene nanofibers, Electrospin 2018 – an International conference,

Wallenberg Research Centre at Stias, Stellnbosch, South Africa, 16th to 18th July, 2018.

10) Murage M., Muge E., Nyokong T., Amuhaya E., Metallo-substituted porphyrins as antimicrobial agents against gram-positive and gram-negative bacteria. 9th International Interdisciplinary conference, Multimedia University, Nairobi, Kenya, June 27th 2019.
11) Oyim J., Murage M., Derese S., Mack J., Nyokong T., Amuhaya E.K., Development of photoactive materials for water decontamination using photodynamic-antimicrobial chemotherapy. 9th International Interdisciplinary conference, Multimedia University, Nairobi, Kenya, June 28th 2019.
12) Scaiano J.C., A Green Road Map for Heterogeneous Photocatalysis, 102nd Canadian Chemistry Conference and Exhibition, Quebec City, June 2019.
13) Scaiano J.C., Canadian Light Source T.K. Sham Award Lecture: Design of Heterogeneous Photocatalysts for Free Radical Generation and for Hydrogen Production: Just a Game of Free Energy Management?, 102nd Canadian Chemistry Conference and Exhibition, Quebec City, June 2019.
14) Wang B., Duke K., Scaiano J.C, Lanterna A.E, Cobalt-Molybdenum Co-Catalyst for Heterogeneous Photocatalysis, International Conference on Photo chemistry, Boulder, Colorado.
15) Scaiano J.C., The many faces of Titanium Dioxide: From H2 generation and water decontamination, to Green Catalysis Inspired by Crop Rotation Practices in Agriculture, International Synthetic Photochemistry Forum, Plenary lecture, Wuhan, China, Nov. 2018.
16) Scaiano J.C., Organic Photocatalysis with Metal-Decorated Titanium Dioxide, Plenary Lecture, IUPAC-24th International Conference on Physical Organic Chemistry, Faro, Portugal, July 2018.
17) Scaiano J.C., The many faces of Titanium Dioxide: From H2 generation and water decontamination, to Green Catalysis Inspired by Crop Rotation Practices in Agriculture, International Synthetic Photochemistry Forum, Plenary lecture, Photo4Future Conference, Eindhoven, the Netherlands, November 2018.
18) Lanterna A.E, Hainer A.S, Fournier K., Vallieres M., Silvero M.J.C., Scaiano J.C. , Solar Strategies for the Simultaneous Photocatalytic Generation of H2, Sterilization and Decontamination of Water, (Plenary lecture) NanoOntario Conference, Carleton University, November 2018.
19) Mapukata S., Nyokong T., Magnetic Nanoparticles Improve Bacterial Photoinactivation Properties of an Asymmetrical Zinc Phthalocyanine towards Stapphylococcus aureus. 11th International conference of Porphyrins and Phthalocyanines (ICPP-11), 28th June – 3 July, 2021 Virtual.
20) Sindelo A., Lanterna A.E, Scaiano J.C., Nyokong T., Covalently Linked to Functionalized Glass Wool for Photocatalysis, 11th International conference of Porphyrins and Phthalocyanines (ICPP-11), 28th June – 3 July, 2021, Virtual.

21) Sindelo A., Nyokong T., Development of Magnetic Nanoparticles-Phthalocyanine Conjugates for Photoinactivation of Bacteria, 11th International conference of Porphyrins and Phthalocyanines (ICPP-11), 28th June – 3 July, 2021, Vitual
22) Oyim J., Amuhaya E., "Photodegradation of levofloxacin in water by porphyrin immobilized on glasswool", Eleventh International Conference on Porphyrins and Phthalocyanines - ICPP-11. Virtual.
23) Murage M., Amuhaya E., Synthesis, photo physical studies, and photodynamic antimicrobial activity of 4-(10,15,20-tris(4-(dimethylamino) phenyl)porphyrin-5-yl) phenol porphyrin and its, Zn and In complexes, Eleventh International Conference on Porphyrins and Phthalocyanines - ICPP-11.
24) Obai T., Mwanzia B., Amuhaya E., Omollo C., 'Cyclodextrin-carboxymethyl cellulose formulation for metalloporphyrin delivery in topical photodynamic antimicrobial chemotherapy (PACT)', Presented at the 10th Kenya Chemical Society International Conferences on 24th June 2022.
25) Bakasa C., Amuhaya E., Muhanji C., Amolo G., 'Exploring Metalloporphyrins Structure for Photodynamic Antimicrobial Chemotherapy Water Treatment Method' Presented at the 10th Kenya Chemical Society International Conferences on 24th June 2022.

b) Symposia/Seminar

1) Vallieres M., Lanterna A.E, Scaiano J.C., 21st Century Medicinal Waters, Does the Sun Do More Than You Think? Physical-Organic Mini-Symposium, Université du Québec à Montréal, Montreal, Canada, November 2018.
2) Scaiano J.C., The many faces of Titanium Dioxide: From H2 generation and water decontamination, to Green Catalysis Inspired by Crop Rotation Practices in Agriculture, Regensburg, Germany 2018.
3) Scaiano J.C., The many faces of Titanium Dioxide: From H2 generation and water decontamination, to Green Catalysis Inspired by Crop Rotation Practices in Agriculture, Munich, Germany 2018.
4) Scaiano J.C., The many faces of Titanium Dioxide: From H2 generation and water decontamination, to Green Catalysis Inspired by Crop Rotation Practices in Agriculture, Distinguised Seminar Lecture, NorthEastern University, Boston, MA, September 2018.
5) Scaiano J.C., The many faces of Titanium Dioxide: From H2 generation and water decontamination, to Green Catalysis Inspired by Crop Rotation Practices in Agriculture, Distinguised Seminar Lecture, NorthEastern University, Boston, MA, September 2018.
6) da Silva D. R.C., Mapukata S., Lanterna A. E., Nyokong T., Scaiano J. C., Development of Metal Oxide Nanofibers as potential antimicrobial agents. Oral presentation. 47th Physical Organic Minisymposium (POMS), York University, November 2019.
7) Fournier K., Oyim J., Amuhaya E., Lanterna A. E., Scaiano J.C., Porphyrin-decorated Glass Wool for Water Remediation. Poster presentation. 47th Physical Organic Minisymposium (POMS), York University, November 2019

8) Amuhaya E. Synthesis, photophysical properties and photodynamic antimicrobial activity of meso 5,10,15,20-tetra(pyren-1-yl) porphyrin and its indium(III) complex, presented during the The University of Nairobi Research Week 26th October 2022. INVITED.
9) Marcus Baumann – Guest speaker at an online seminar attended by the three research groups, June 19th 2020. About 50 participants.
10) Graca Vicente – Guest speaker at an online seminar attended by the three research groups, July 24th 2020. About 50 participants.
11) Austin Aluoch – Guest speaker at an online seminar attended by the Kenyan research group June 24th 2021.
12) Adedayo Fashina – Guest speaker at an online seminar attended by the Kenyan research group July 9th 2021.

As part of the training, throughout the project duration, each of the three research groups held regular group meetings in which students gave research progress and literature talks.

c) Workshops

1) First grant-related workshop "Light-matter interactions,"took place in Nairobi (Feb. 22- Mar. 2) with Lanterna, Nyokong and Scaiano as lecturers at USIU-Africa, February 27th – March 1st 2018 with about 20 students.
2) A presentation was also made to Senior Administrators at United States International University-Africa, February 27th – March 1st 2018.
3) Amuhaya E., 'The STEM Gap' presented during the 'Developing a Career as a Woman Scientist: Challenges and coping strategies by female chemists in Kenya at USIU-Africa, on 24th February 2022.INVITED.
4) Amuhaya, E., 'Development of Photoactive Materials for Water Decontamination' presented at the 'Antimicrobials: Approaches in Drug Development and Drug Delivery Research' workshop held at USIU-Africa, on 31st March, 2022.

iii) Capacity building

One of the main expected outputs of the projects was to build capacity of researchers through training of students at the undergraduate, masters and doctoral levels. During this project period, a total of 10 PhD, 10 MSc and 11 Undergraduate students were trained. Of these, 2 PhDs, 8 Msc and 11 undergraduate students have since graduated. The remaining students are at different stages of their studies. In a bid to help close the gender gap in STEM programs, the three research groups made deliberate efforts to recruit and train female students. Of all the trained students, 18 (58%) were female, while the remaining 13 (42%) comprised of male students.

Below is a list of students who have been trained under the project. The list includes those who have since completed their studies and those who's studies are still ongoing.

Name/Home Institution	**Level**	**Status of training**	**Gender**	**Supervisors**
James Oyim	PhD	In progress	M	Prof. Nyokong/Dr. Amuhaya

Rhodes University/USIU-Africa				
Margaret Murage University of Nairobi/USIU-Africa	PhD	Completed Awaiting thesis defense	F	Dr. Amuhaya
Sebastian Oloo University of Nairobi/USIU-Africa	MSc	Completed	M	Dr. Amuhaya
Jackline Khisa University of Nairobi	MSc	Completed	F	Dr. Amuhaya
Abraham Samoei* Kenyatta University/USIU-Africa	MSc	Dropped out	M	Dr. Amuhaya
Reuben Kamuri** Kenyatta University/USIU-Africa	MSc	Dropped out	M	Dr. Amuhaya
Patrick Kinuthia University of Nairobi/ USIU-Africa	MSc	Completed Awaiting thesis defense	M	Dr. Amuhaya
Kelvin Warui University of Nairobi/USIU-Africa	MSc	Completed Awaiting thesis defense	M	Dr. Amuhaya
Carolyne Bakasa Technical University of Kenya/ USIU-Africa	PhD	In progress	F	Dr. Amuhaya
Bernard Mwanzia Technical University of Kenya/USIU-Africa	PhD	In progress	M	Dr. Amuhaya
Rose Ndung'u USIU-Africa	Undergraduate	Completed	F	Dr. Amuhaya
Lisa Irungu USIU-Africa	Undergraduate	Completed	F	Dr. Amuhaya
Ketty Otenyo	Undergraduate	Completed	F	Dr. Amuhaya

USIU-Africa				
Faith Makau USIU-Africa	Undergraduate	Completed	F	Dr. Amuhaya
Tiffany Obai USIU-Africa	Undergraduate	Completed	F	Dr. Amuhaya
Vivian Ngugi USIU-Africa	Undergraduate	Completed	F	Dr. Amuhaya
Sophia Riugu USIU-Africa	Undergraduate	Completed	F	Dr. Amuhaya
Sonia Thuita USIU-Africa	Undergraduate	Completed	F	Dr. Amuhaya
Sarafina Saru USIU-Africa	Undergraduate	Completed	F	Dr. Amuhaya
Sivuyisiwe Mapukata Rhodes University	PhD	Completed	F	Prof. Nyokong
Samuel Shabangu Rhodes University	MSc	Completed	M	Prof. Nyokong
Azole Sindelo Rhodes University	PhD	Completed	F	Prof. Nyokong
Collen Makola Rhodes University	Msc	Completed	M	Prof. Nyokong
Morgan Vallieres Univeristy of Ottawa	Undergraduate	Completed	F	Prof. Scaiano
Kelsey Fournier University of Ottawa	MSc	Completed	F	Prof. Scaiano
Andrew Hainer University of Ottawa	PhD	In progress	M	Prof. Scaiano
Daliane Regis Correa da Silva University of Ottawa	PhD	In progress	F	Prof. Scaiano
Connor Bourgonje University of Ottawa	PhD	In progress	M	Prof. Scaiano
Sara Currie University of Ottawa	Summer student	Completed	F	Prof. Scaiano
Teresa Gawargy	Summer student	Completed	F	Prof. Scaiano

University of Ottawa				
Sara Currie University of Ottawa	MSc	In progress	F	Prof. Scaiano
Nelson Rutajoga University of Ottawa	PhD	In progress	M	Prof. Scaiano

*when all institutions of learning closed in Kenya, during the COVID-19 pandemic, the student did not return

**student left the program due to multiple reasons including family and financial constraints.

The IDRC trilateral program enhanced the training environment for the students. In February 2018, during a workshop held at USIU-Africa, the graduate students had a chance to meet Profs. Nyokong and Scaiano, who are prominent in their areas of research. Through a series of lectures over an entire week offered by Prof. Nyokong, Prof Scaiano and Dr. Lanterna, the Kenyan students learnt more about other aspects of their research work, which included photocatalysis, photochemistry and nanotechnology.
In the Kenyan research group, students that studied under the program had no prior experience in organic synthesis, but all of them learnt how to synthesize, purify and carry out some photophysical and antimicrobial analyses. This was made possible through the funds from the project, which facilitated the purchase of lab equipment eg UV-Vis spectrometer, spectrofluorometer, fume hood, shaking incubator etc.

iv) Staff and Student exchanges

The project facilitated the exchange of staff and students to further enhance the learning experience. A total of 14 visits took place. The table below provides a summary of these exchanges and the duration of each visit.

	Name	**Place Visited**	**Period of Stay**
1.	James Oyim	Rhodes University, South Africa	1 month
2.	Sebastian Oloo	University of Ottawa, Canada	3 months
3.	Sivuyisiwe Mapukata	University of Ottawa, Canada	3 months
4.	Prof. Scaiano	USIU-Africa	1 week
5.	Dr. Lanterna	USIU-Africa	1 week
6.	Prof. Nyokong	USIU-Africa	2-3 days
7.	Samuel Shabangu	USIU-Africa	1 month
8.	Kelsey Fournier	USIU-Africa	1 month
9.	Margaret Murage	Rhodes University, South Africa	2 months
10.	Daliane Regis	Rhodes University, South Africa	3 months
11.	James Oyim	University of Ottawa, Canada	3 months
12.	Azole Sindelo	University of Ottawa, Canada	3 months
13.	Collen Makola	USIU-Africa	1 ½ months

The student exchange visits ensured students from the three research groups learnt skills from a different research group. This subsequently led to a lateral knowledge and skill transfer to those who did not manage to travel. Unfortunately, the emergence of the COVID-19, and the subsequent travel restrictions prevented any further exchanges among the research groups. However, through the collaboration, samples were shipped from Kenya to South Africa for analyses. This ensured continuity of the project.

v) New and Ongoing Collaborations

During the duration of the project, new collaborations were established, and some ongoing ones. Below are the collaborations that participated in the project.

	Name	Institution	Description of joint activities
	Prof. A. Yu. Tsivadze/ Prof. Gorbunova (Ongoing)	Frumkin Institute of Physical Chemistry and Electrochemistry of Russian Academy of Sciences	Synthesis of Porphyrin type complexes
	Prof. Z. Shen (Ongoing)	Nanjing University	Synthesis of Porphyrin type complexes
	Luzchem Research, Inc (Ongoing)	Industry	Prototype testing at uOttawa
	Univ. Cordoba, Argentina (New)	MINCyT	Design of advanced materials for hydrogen generation using visible light
	Dr. Holiness Nose (New)	Technical University of Kenya	Computer aided design of porphyrin complexes
	Dr. Jan Dusza (New)	Institute of Materials Research of Slovak Academy of Science	Manufacture of ceramic catalytic materials
	Prof. Anabel Lanterna (Ongoing)	University of Nottingham, UK	Catalyst design for photochemistry and photoelectrochemistry
	Dr. Albert Ndakala (Ongoing)	University of Nairobi	Stereochemistry, synthesis
	Prof. Graca Vicente (Ongoing)	Louisiana State University	Synthesis, cytotoxicity studies
	Prof. George Omolo (New)	Technical University of Kenya	Molecular modeling
	Dr. Clare Muhanji (New)	Technical University of Kenya	Synthesis, stereochemistry
	Dr. Dr. Franscisco Martin-martinez (New)	Swansea University	Molecular modeling

vi) Activities/ Events and articles for Broader Visibility

1) Kenya's USIU-Africa Professor Awarded with a Nanotechnology Research Grant, Techweez, July 11th 2017
2) Chemistry professor to receive large research grant to study nanotechnology, Campus This Week, July 7th 2017
3) USIU to Improve Research from Trilateral Partnership Initiative, Capital campus, July 12th 2017
4) Initiative aims to use nanotechnology to purify water, Nano, August 16th 2017
5) Africa-Canada scheme funds nanotech to purify water, Sciedev, August 17th, 2017
6) IDRC Trilateral research chairs seminar, February 26th 2017, USIU-Africa
7) The project highlighted as part of Western Alumni Gazette (WAG), with the title" Tebello Nyokong – shepherd to researcher" Western University, London Ontario Canada
8) Prof. Tebello Nyokong Awarded Degree of Doctor of Science, Honoris Causa from Western University, London, Ontario, Canada (June 2019)
9) T. Nyokong received the Linstead lifetime Career Award on phthalocyanine chemistry during 11th International conference of Porphyrins and Phthalocyanines (ICPP-11), 28th June – 3 July, 2021, Virtual
10) Scaiano J.C., received the T.K. Sham Award during the 102nd Canadian Chemistry Conference and Exhibition, Quebec City, June 2019
11) Scaiano, J.C. received the Nick Turro Award from the Interamerican Photochemical Society, Fort Lauderdale, USA, Jamuary 2020.

vii) Unexpected Outcomes

In the course of the project's implementation, there were some unexpected outcomes. These included scientific outcomes, changes in behaviors, and new practices. These were:

1) Development of new catalysts based on black TiO_2 that operate with visible light to degrade organic contaminants and kill bacteria.
2) Incorporation of new mateials to the synthesized porphyrin metal complexes eg hydrogels to improve the solubility and antimicrobial properties of the porphyrins.
3) Incorporation of molecular modelling in designing molecules with enhanced antimicrobial properties.
4) Following the successful research outputs of the first pair of undergraduate students recruited into the project, there has been an increase in number of undergraduate students showing interest and participating in the project over the years.
5) One undergraduate student has applied to graduate schools in the US, with the intention to pursue their graduate studies in a related research area.
6) Using NRF funds from the project, the south African group purchased equipment such as lasers and TG essential for the project.
7) The Kenyan research group utilized IDRC funds to purchase several lab equipment, eg UV-Vis spectrometer, Spectroflurometer, fume hoods, etc, which enabled the research to progress with more ease and independence.

viii) Funding applications submitted and awarded

In the course of the project's implementation, the chairs applied and were awarded more funding by different agencies. These augmented the research and allowed for more collaborations with other researchers. Below is a list of the grants:

1) Funding organization: United States International University-Africa Internal grant
   Applicant(s): Edith Amuhaya, Betty Mbatia, Naumih Noah and Eugene Otoo
   Title: Development of Photoactive Materials for Water Decontamination
   Value: Ksh. 1,000,486 (approx. 13,000 CAD)
   Time period: 15 months
2) Funding organization: MINCyT (Argentina) and University of Ottawa
   Applicant(s): Dr. Juan Scaiano and Dr. Gabriela Lacconi
   Title: Design of advanced materials for hydrogen generation using visible light.
   Value: 22,500 CAD
   Time period: 2 years
3) Funding organization: Natural Sciences and Engineering Research Council of Canada
   Applicant(s): Dr. Juan Scaiano
   Title: Lignin coating technology for health and cosmetics applications
   Value: 123,800 CAD
   Time period: 1 year
4) Funding organization: Department of Science and Technology/Mintek Nanotechnology Innovation center
   Applicant(s): Tebello Nyokong
   Title: Development of nanoparticles for detection of pollutants
   Value: R 2 500 000 (approx. CAD 230 000)
   Time period: 1 year
5) Funding organization: Kenya Education Network (KENET)
   Applicants: Dr. Holiness Nose, Dr. Edith Amuhaya and Dr. Betty Mbatia
   Title: Computer-aided design and Development of Porphyrin-based Photosensitizers for Water Purification
   Value: Value: Ksh. 1,500,000 (approx. 19,000 CAD)
   Time period: 1 year

Project Management Processes

The project, which involved three research chairs from three different countries, required excellent and timely communication as well as aligning of schedules in order to ensure the planned activities progressed seamlessly. In addition to the planned lab based research, other activities included student exchange visits, writing of research articles, sample analyses as well as writing of the annual technical reports. Being a young research group, the Kenyan group benefited immensely from this collaboration, through knowledge transfer and access to specialized equipment that were not available at its institution. In USIU-Africa, there was general improvement in processes which enabled the project to progress with ease.

Below are detailed descriptions of the processes that were involved in managing the project.

i) Early on in the project, conversations were held regarding IP policies involving the three universities. IP officers from each institution developed an MOU on IP which was signed between the three institutions.

ii) There was effective communication between the research chairs when planning student exchange visits, which ensured students traveled at a time agreed upon by all three chairs.
iii) Realizing that only large scale flow techniques will provide a scalable solution for water decontamination, the group at uOttawa initiated a collaboration with researchers in Slovakia who specialize in the field of ceramics, in the hope that porous ceramic materials, combined with the fibrous TiO_2 manufactures in South Africa would provide an integral solution for scaled up solar water purification.
iv) Following the outbreak of the COVID-19 pandemic and the subsequent travel restrictions, the collaborations in the project provided the opportunity to send samples from the Kenyan research group to South Africa for analyses. This ensured project continuity and progression in student studies.
v) The existence of MoUs between university of Nairobi, Kenyatta University and Technical University of Kenya enabled graduate students to formally carry out their research activities at USIU-Africa and have access to all the available resources. Through USIU-Africa Human resources and finance offices, the students were able to receive their monthly stipends and without delays.
vi) At USIU-Africa, several guidelines were developed. These are:
    1) Online safety training module for graduate students before the start of their lab work. Additionally, USIU-Africa's OSHA office organized and conducted a safety training seminar for the school where the project was housed (ie School of Pharmacy and Health Sciences).
    2) Waste management handbook, which outlines clear instructions and procedures on how to handle waste that is generated in the lab, while protecting the user and the environment.
    3) Spills and leaks log sheet, which is referenced in the safety training module, and is available in the labs for reference during emergencies.
    4) Emergency treatment plan, which is referenced in the safety training module and is also available in the labs for reference during emergencies.
    5) Emergency action plan, which outlines the safety procedures to be taken during an evacuation following an emergency. It is referenced in the safety training module and is also available in the labs for reference during emergencies.
vii) At USIU-Africa, the institutional management and monitoring of funds ensured verifications are carried out at every level, from requests to procurement to payments.
viii) At USIU-Africa, procurement of equipment was achieved through existing university policies and processes. Additionally, the Kenyan research chair was allowed to make all decisions regarding preferred equipment specifications based on the intended use.
ix) Purchase of large equipment at USIU-Africa was done after consultations with the other two research chairs, who have more experienced and based on the expected outputs.
x) At USIU-Africa, implementation of electronic data management system led to improved processing of requests for lab supplies.
xi) A new program, MSc Pharmaceutical Chemistry was proposed, and the concept note approved at the school and senate level of the institution. The development is currently in the final stages of development.
xii) Following the outbreak of the COVID-19 pandemic, the three institutions implemented COVID-19 guidelines which enabled students to return to the lab for their research activities.

xiii) One student, James Oyim, managed to move to Rhodes University to join the South African research group, where he is currently continuing with his research under joint supervision of Prof. Nyokong and Dr. Amuhaya.

Challenges Experienced in the Project

Just like any other project, this project faced some challenges. Below is a description of challenges that were faced.

i) At USIU-Arica

1. There were delays in delivery of items. This is because most of the reagents used in the project were specialized chemicals and therefore not readily available in the country. Sometimes the delays could take months to be delivered and even with early planning, this was a recurring problem. This became a major limitation especially where there was need to change procedures to new ones which required different chemicals.
2. Delays in deliveries was also experienced whenever vendors supplied the wrong items. This meant either contacting a different vendor to supply the item, or starting the procurement process all over.
3. At the beginning of the project the Kenyan government made changes in the importation of chemicals and reagents, which required vendors to provide additional information before chemicals were allowed into the country. This also resulted in delays in deliveries.
4. In Kenya, it was challenging to attract female students at the MSc level. This was mainly due to an overall low female enrollment into the masters' programs across the country.
5. During the COVID-19 pandemic, all institutions of learning, including USIU-Africa, were closed indefinitely. This meant no research work took place during this period.
6. Also as a result to COVID travel restrictions, there were delays in processing and delivery of items by vendors, since most of the reagents had to be imported.
7. During the COVID-19 pandemic, it was challenging to engage some of the students due to unreliable internet connectivity. Online group meetings and presentations were therefore far in between.
8. One student left during the pandemic and attempts to reach him have been unsuccessful, with calls going unanswered.
9. Upon the partial resumption of research activities, delays were experienced whenever a student/personnel tested positive for the coronavirus. The individual had to remain in quarantine for a minimum period of 2 weeks, or until they tested negative. This affected research progress as well as writing and submission of annual technical and annual reports.
10. While IDRC extended the project duration by 6 months, to allow the testing of toxicities of synthesized molecules, it was impossible to do this because the project did not get the necessary funding from the university.
11. Earlier this year, system failure across the university led to delays in compiling reports and also completing all pending payments on time.

12. Development of MSc. Pharmaceutical Analysis program experienced delays during the pandemic, because it was challenging to get feedback and participation from different stakeholders. Additionally, upon further consultations, it was agreed that the school develops an MSc Pharmaceutical Chemistry course instead of MSc. Pharmaceutical Analysis. The school considered the wider prospects of getting students enrolled into the program, and the inclusion of a wider variety of techniques in the MSc. Pharmaceutical Chemistry program. The program is still under development.

ii) At Uottawa
    1. There was potential loss of Teaching Assistant stipends for the terms in which Ottawa students travel to Africa, with a potential replacement funding of about $5K per student per term.
    2. Impact of the COVID-19 pandemic led to delay in research. There was a shut down for 3 months, then at 33% lab time, followed by about to 66% lab time. Under these conditions, there are were major problems with services, some not available, some not hands-on. The switch to more assisted services meant delays and increased costs.
    3. Impact of Anabel leaving to the UK on the UOttawa portion of the project: Anabel played a major role from the day we started writing the research proposal. While her interests in the project continued, her new responsibilities at Nottingham understandably limited her discussions and participation.

iii) Across the three institutions
    1. The main challenge for all three institutions related to university closures, extremely limited return to research, and the closure or borders and limitations to travel caused by the COVID-19 pandemic. All three groups have made major efforts to retain the engagement and enthusiasm of students and achieve whatever limited progress was possible in the first half of 2020.
    2. The second effect had to do with student (and faculty) exchanges which ground to a halt during and after the pandemic. This was a result of the travel restriction and the potential risk of students and faculty contracting the virus while away from their home country.

Resources and Institutional Context Relating to the Kenyan Chair

This project has had a major impact on the Kenyan research chair's career as an upcoming researcher in academia. Below is a detailed description of ways the project was beneficial as well as the support the chair received from her institution.

1. The Kenyan chair received the full support of the institution. This was not only in the form of university resources, but also by the university reducing her teaching load. Through the funds, the research lab was equipped leading to improved quality of research conducted. The major equipment purchased through the grant included a fume hood, UV-Vis spectrometer, spectrofluorometer, and rotary evaporator. This equipment not only made it convenient to carry out research work leading to high quality research training, but it also ensured the research group worked independently without heavily relying on the limited resources available in the school. Other lab renovation work in the lab was done to install extra bench space and drawers.

2. The project has made it relatively easy to attract both graduate and undergraduate students. This was because of the quality of research, and also because the project funded the research in totality, from chemicals and reagents, to equipment, to conference attendance, monthly stipend and research visits to SA and Canada. This removed the financial burden from the students, and enabled them just focus on the research.
3. The university implemented an electronic data management system at the institution, which led to improved processing of purchase requests for lab supplies, making it faster and smoother.
4. In terms of career growth, the project has led to exponential growth. Following the student supervision as well as publications, the Kenyan chair qualified for promotion to the rank of Associate professor. Without the project, the collaborations and the funding, this would have taken much longer.
5. The Kenyan chair was invited to join the prestigious Kenya national Academy of Sciences. This is a society that is composed of the top researchers in Kenya.
6. In 2022, the Kenyan chair was appointed to the regional research and Development working group (Resource Mobilization sub-committee) of the East African Science and Technology Commission of the East African Community. This was based on her research credentials as well as ability to attract research grants, with IDRC's Trilateral Research chair initiative being the largest grant she ever won and managed.
7. The Kenyan chair has also been acknowledged as a Kenyan Female scientist who has overcome numerous hurdles to make it in the research world. In 2022, she was invited to give a talk on the 'STEM gap'.
8. Currently she is involved in a mentorship hub which aims to mentor young women in Kenya who are starting their careers in research.
9. When the Kenyan chair first started carrying out research at USIU-Africa, there was limited understanding about the complexities of conducting scientific lab based research. This ranged from procurement processes, to hosting of visiting students, to gaining access to the labs for graduate students who were registered in other universities. All these efforts made it easier for colleagues who are also carrying out their research activities, because the processes are now better understood by the administration.

Conclusion

The Trilateral Research Chairs Initiative was a successful project that not only helped strengthen research ties among the three countries, but also help generate materials that have great potential in water decontamination, a problem that is especially rampant in Africa. Furthermore, through this project, a high number of students have been trained, and in this way, increasing the number of skilled personnel in research.