FEDERAL UNIVERSITY OF AGRICULTURE
ABEOKUTA NIGERIA

78th INAUGURAL LECTURE

NANOTECHNOLOGY: THE SIZE-POWERED HARBINGER OF THE 21ST CENTURY TECHNOLOGICAL REVOLUTION

by

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FUNAAB INAUGURAL LECTURE
Series No. 78

Wednesday June 21, 2023

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The 78th Inaugural Lecture was delivered under the Chairmanship

of

The Vice-Chancellor

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B.Sc (Agric Biology); M.Sc (Crop Improvement),
Ph.D (Ibadan), FGSN, FAIMP, FIHSC

Published Wednesday June 7, 2023

ISBN:978-978-799-092-6

FUNAAB INAUGURAL LECTURE SERIES

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NANOTECHNOLOGY: THE SIZE-POWERED HARBINGER OF THE 21ST CENTURY TECHNOLOGICAL REVOLUTION

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1.0 PREAMBLE

I am indeed grateful to God for the grace given me to stand before you today to present the 78th Inaugural Lecture of the Federal University of Agriculture, Abeokuta. This is the 3rd Inaugural Lecture from the Department of Chemistry and the 5th from the College of Physical Sciences (COLPHYS). This is the first inaugural lecture from the first Professor of Nanotechnology in Nigeria and serves an honor and recognition that this is coming from nowhere else other than the Department of Chemistry, Federal University of Agriculture, Abeokuta, Nigeria. However, I must note it with recognition and honour that Lateef Agbaje, a friend, great nanotechnology scholar and a Professor of Microbiology from LAUTECH had previously given inaugural lecture centered on Nanobiotechnology. The inaugural lecture presentation of today is a collection of all aspects of nanotechnology (Nanomaterials, nanocomposites, nanohybrids, nanoporous membranes, nanosensors, nanomedicines, nanoengineering, nanobiotechnology, nanoagriculture, nanocomputation e.t.c) in which I have made significant contribution to knowledge.

Mr. Vice Chancellor, Sir, if I decide to summarize my contributions to knowledge covering all nanos as reflected in my over 100 publications and several patents, we may spend the whole day here. Therefore, Sir, permit me to cover only areas of nanotechnology where I have made innovative and inventive contributions with evidence of prototypes and technology useful to mankind.

2.0 INTRODUCTION

2.1 Chemistry as a blueprint for nanotechnology revolution

Chemistry is the study of substances their properties, structure, and the changes they undergo. Chemistry is a big part of daily life. Literally, everything we enjoy today has been improved by chemistry. Chemistry is the bedrock for scientific and technological development. Chemistry can explain almost all reactions taking place in nature. With the help of chemistry, we are able to make new substances such as medicine that help us in maintaining good life. Chemistry holds the key to manufacturing new compounds and materials. Nanotechnology owes a lot to chemistry because chemistry is essential in synthesizing nanoscale structures and devices. The tools of chemistry can guide nano developments. A "strong marriage" between nanotechnology and the principles and practices of chemistry holds the key to open new avenues in the field of nanotechnology which are not yet fully explored. In the chemical industry sector, nanomaterial (NM) are applied based on their special catalytic properties in order to boost energy and resource efficiency and nanomaterial can replace environmentally problematic chemicals in the fields of application. Hence, nanotechnology brings a transition from classical engineering concepts to chemical assembly. Nano technology is, therefore, a linking field between chemistry and engineering.

It can be recalled that chemistry is the branch of science that deals with the study of composition, structure and properties of matter (comprises all things that have weight and occupy space) together with the associated changes (chemical and /or physical) and such changes impact on the welfare of man and society. Chemistry can thus be considered as the study of everything, as there is nothing on earth that is not matter, and hence chemistry.

The fact that chemistry is the central science and science is the foundation on which technology is built, buttresses the central position of chemistry in technology (i.e. all forms of technology) including nanotechnology. Chemistry is also an art, by its very essence, its ability to create. Chemistry actually fashions out new worlds that were not in existence.

2.1.1 *Impact of Chemistry in Nanotechnology*

Chemistry is dealing with atoms and molecules, with great attention laid on their arrangement. Therefore, it seems to be the paradigm of the vision of Nanotechnology - to build up new structures, atom by atom. Nano systems and molecular devices that are used in nanotechnology require more than just the covalent chemistry feature because such system may contain several thousands of atoms. This is where intermolecular interactions play vital role. They can help to combine individual molecules into complex assemblies called supra molecular structures. The emergence of supra molecular chemistry has had a profound effect on how efficiently chemists prepare structures of different sizes and shapes with dimension in the range of 1 to 100 nm using spontaneous secondary interactions such as hydrogen bonding, dipole-dipole, charge transfer, Vander Waals, and $\pi-\pi$ stacking interactions (Eluchie, 2018**;** Crichton and Harper, 2003). The said methods would utilize the concept of molecular self-assembly and/or supra molecular chemistry to automatically arrange atoms and molecules into useful conformation through a bottom-up approach which seek to arrange smaller components into more complex assemblies. Also, in synthetic chemistry, self-assembly has made recent advances in the area of supra molecular chemistry which are divided into three main fields (organic chemistry, inorganic chemistry, and polymer chemistry). This bottom-up approach that has been used to construct nanostructures is advantageous over the bottom-down approach such as microlithography which requires substantial effort to fabricate microstructures and devices as the target structures are extended to the range below 100 nm.

Therefore, there is an increasing realization that the bottom-up approach would open a route to nanostructures that are currently inaccessible by the top-down approach. Thus far, the development of the bottom-up methods to create nanostructures has been inspired primarily by Nature, which displays a wide variety of complex nanostructures with astonishing precision (Rebek, 1990). These Nano scale structures in biological systems are specifically put together from two or more small molecular components by means of secondary interactions. The precision and specificity are indicative of control and directionality displayed by secondary interactions between complementary components in biological systems. In addition, the bottom-up approach benefits from having thermodynamic minima in its resulting nanostructures due to the reversible nature of secondary interactions. Obviously, the challenge is to synthetically create nanostructures with such precision and specificity as seen in biological systems by cleverly incorporating complementary recognition sites in the molecular components for secondary interactions. This challenge is only met by, first, understanding how molecular self-assembly in biological systems operates to generate well-defined aggregates and then, transferring the knowledge learned from biological systems to chemical synthesis chemistry. Molecular chemistry establishes its power over the covalent bond, while beyond molecular chemistry lies the field of supra molecular control over the intermolecular bond. Supramolecular chemistry is an interdisciplinary field that deals with interaction between molecules, how they can recognize each other, assemble and function on a molecular scale. It provides a bottom-up approach Nanoscale system with applications covering chemical, physical, material and biological features. Supramolecular chemistry methods are widely used in chemical analysis, medicine, catalysis, and photochemistry. Supramolecular structures form the basis for a great number of biologically active substances, the creation of photo and chemo sensors, molecular electronic devices, the development of Nanocatalyst, the system of materials for nonlinear optics and the simulation complex biological complexes (Biomimetic).

2.2 History of nanotechnology and material science

Figure 1 expresses various fundamental nanotechnology champions starting from its predictions and miniaturization of electronics.

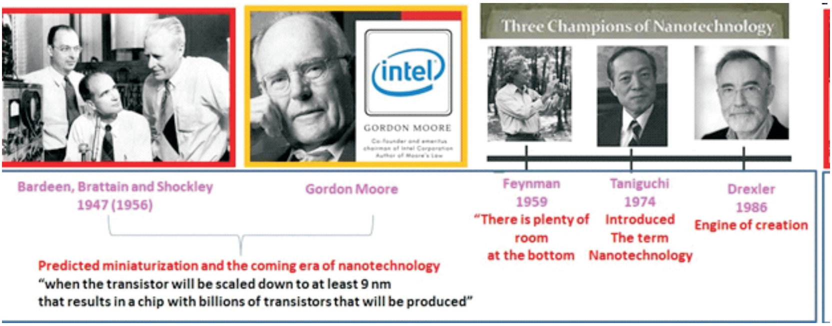

Figure 1: Nanotechnology champions and pre-nanotechnology predictions

In the year 1950, the television was black and white with lower picture quality. There was no internet, cell phones, and computer. Today, we all are enjoying all these things because of silicon chips. Development in the field of Nanotechnology brings all these things to the benefit of humanity. The first transistor was designed in 1947 by Bardeen, Brattain, and Shockley (Riordan *et al*. 1999) for which they received a Nobel Prize in 1956. Later on, in 1951 silicon-based transistor was produced and then the integrated circuit was created in 1958. Finally, Gorden E. Moore became one of the founders of Intel in 1965. He established a law called Moore's Law (Moore, 1998). In 1965, there were 30 transistors in a single chip, then in 1971, the number became 2000. Now, this number increased to 40,000 transistors. According to the National Nanotechnology Initiative (NNI), when the transistor will be scaled down to at least 9 nm that results in a chip with billions of transistors that will be produced. Huge advantage of Pentium-4 over IBM-360 have been achieved by a miniaturizing of integrated circuits and fabricating of microchips containing ca. $\sim10^9$ units/cm^2 of ~200nm in size. Although study on materials in the nanometer scale can be traced back to centuries, the current fever of nanotechnology is at least partly driven by the ever *shrinking of devices* in the semiconductor industry. The continued decrease in device dimensions has followed the well-known *Moore's law* predicted in 1965. The trend line illustrates the fact that the transistor size has decreased by a factor of 2 every 18 months since 1950. There are many nanoscale electronic devices available now: tunneling junctions; devices with negative differential electrically configurable switches; carbon nanotube transistor; and single molecular transistor; ultrahigh density nanowires lattices and circuits with metal and semiconductor nanowires; etc. Devices have also been connected together to form circuits capable of performing single functions such as basic memory and logic function. Computer architecture based on nanoelectronics (also known as nanocomputers) has also been intensively studied.

These great inventors predicted the coming era of miniaturization, a rudimental fact underpinning nanotechnology.

2.2.1 Feynman's Idea: Entry of Nanotechnology in Modern Science

Richard Feynman was the American physicist who gave the lecture -"There's Plenty of Room at the Bottom" at a meeting of the American Physical Society on December 29, 1959.

Manipulation of individual atoms is a more powerful form of synthetic chemistry than the forms which were used at that time. Initially his talk was unnoticed. In 1990 it was rediscovered and published. Feynman considered a number of interesting things to manipulate matter at the atomic scale. He also suggested that it is possible for us to arrange atoms as we want and then carry out the chemical synthesis by mechanical manipulation. He also discussed the possibility of -swallowing the doctor, a concept which involves building a tiny, swallow-able surgical robot. Moreover, he proposed an experiment to build a set of one-quarter-scale manipulator hands slaved to the operators' hands to build a one-quarterscale machine tool found in any machine shop. The small hands can use these small set of tools to build and operate ten sets of one-sixteenth-scale hands and tools so that billions of tiny factories can be used for specific operations (Madhuri, 2019)

As size gets smaller and smaller, a person can redesign some of the tools due to the relative changes in various forces, namely gravity, becoming unimportant; i.e., it has no importance at that small scale or size. Van der Waals attraction and surface tension becomes more important at smaller scale or size. Feynman stated this point in his talk, yet no one has attempted it in experiments; however, it has been found that some enzymes and their complexes, usually ribosome, function chemically according to his vision. In his talk, Feynman also mentioned that due to their greater uniformity the use of glass and plastic may avoid problems at very small scale. Feynman concluded his talk with two challenges. The first challenge was constructing a tiny motor, and the second one was scaling down letters small enough so as to fit the entire *Encyclopedia Britannica* on the head of a pin. Nowadays, many scientists are interested in nanotechnology.

The development of various techniques/methods in all the fields of science, i.e., physical, chemical, biological and engineering, are aware of the quote of Nobel laureate Richard Smalley,- “Just waitthe next century is going to be incredible. We are about to be able to build things that work on the smallest possible length scales, atom by atom. These little nano things will revolutionize our industries and our lives”.

2.2.2 *Drexler's Engines of Creation*

In 1979, Eric Drexler, after encountering Feynman's talk on atomic manipulation and nanofactories, authored the most important book about nanotechnology, *Engines of Creation: The Coming Era of Nanotechnology,* which was published in 1986. In this book, he introduced the concept of molecular manufacturing to the public (Madhuri, 2019). The history of contemporary nanotechnology traces the development of the concepts and experimental work falling under the broad category of nanotechnology.

In 1981, Drexler's article, -"Molecular Engineering: An Approach to the Development of General Capabilities for Molecular Manipulation" was published in *Proceedings of the National Academy of Sciences of the United States of America*. Again, in 1992, Drexler published Nanosystems, a technical work outlining a way to manufacture extremely high-performance machines out of molecular carbon lattice.

2.2.3 *Impetus given by SEM, TEM and AFM*

The emergence of nanotechnology in the 1980s was caused by the convergence of experimental advances such as the invention of the scanning tunneling microscope in 1981. The scanning tunneling microscope, an instrument for imaging surfaces at the atomic level, was developed in 1981 by Gerd Binnig and Heinrich Rohrer at the IBM Zurich Research Laboratory, for which they received the Nobel Prize in Physics in 1986. Some of the limitations in microscopy were eliminated through the 1986 invention of the atomic force microscope (AFM). Using contact to create an image, this microscope could get an image from non-conducting materials such as organic molecule. Though a scanning electron microscope (SEM) can achieve resolution better than one nanometer, usually, in practice, SEM gives good resolution for particles larger than about 5 nm. For particles smaller than 5 nm, a transmission electron microscope (TEM) gives better resolution.

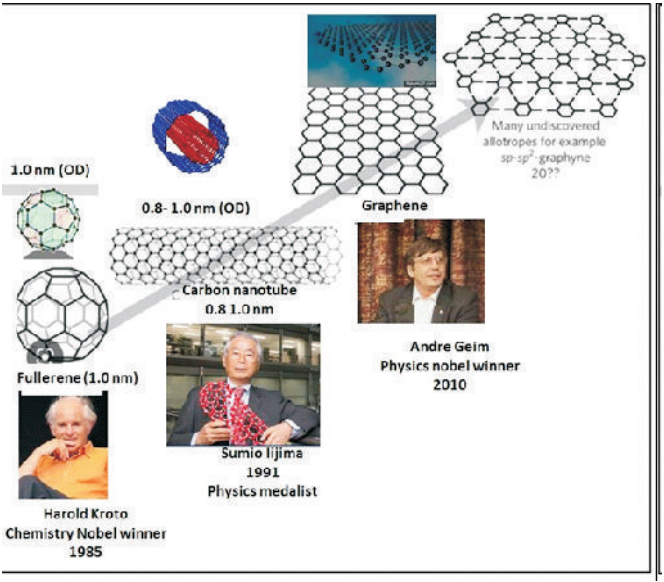

Figure 2: Discoverers of the first generation nanomaterials

2.3 Emergence of first generation nanomaterials

Prior to 1985, we knew about only two carbon allotropes: 1) Graphite (softest material) and 2) Diamond (hardest material). But after the discovery of fullerene by Kroto *et al*.(1985), it is well known that carbon has three allotropic forms, namely diamond, graphite and fullerene, that led to the discovery of nanoforms of carbon. Fullerene became the first fabricated nano form of carbon. Figure 2 indicates progressive discoverers of the first generation nanomaterials.

2.3.1 *Fullerene: The First Fabricated Carbon Nanomaterial*

Advances in surface science have led to studies of clusters, first in considering chains of carbon atoms, then rings of carbon atoms as large as 15-carbon-atom rings. A team at the Exxon Research Laboratory in New Jersey (U.S.A.) succeeded in making large clusters of carbon atoms and published their interesting result in 1984. It was in 1985 when Kroto, Smalley and Curl independently explained the occurrence of these two characteristic phenomena by proposing the formation of large highly symmetrical molecules which they called fullerenes, with 60 carbons at the vertices of regular truncated icosahedrons similar to the structure of a soccer ball (Figure 2). A year later, in late August of 1985, Kroto participated in the laser vaporization experiment with graphite in Houston, Texas (Kroto *et al.*,1985). The Smalley apparatus involved the laser vaporization of a rotating graphite disc in the presence of a helium flow (using a Nd:YAG 532 nm laser). Kroto and the Rice University researchers obtained a mass spectrum exhibiting two main groups of carbon clusters: 1) those with low mass (G 30 carbon atoms) with both odd and even numbers of carbon atoms; and 2) high mass clusters (>36 atoms) showing only even numbers of carbon atoms.

2.3.2 *Carbon Nanotubes*

Carbon nanotubes (CNTs) are one of the most extensively studied carbon nanomaterials (CNMs). Carbon filaments less than 10 nm in diameter were prepared in the 1970s and 1980s through the synthesis of vapor-grown carbon fibers by the decomposition of hydrocarbons at high temperatures in the presence of transition metal catalyst particles of <10 nm diameter. However, no detailed systematic studies of such very thin filaments were reported in these early years. It was not until the observation of CNT in 1991 by Sumio Iijima of NEC Corporation in Japan that carbon nanotubes were discovered using high-resolution transmission electron microscopy (HRTEM), in which the carbon ring-like structures are extended from spheres into long tubes of varying diameter (Iijima, 1991) that the CNT study was seriously launched. The quest for fabricating various nanoforms of carbon has resulted in the formation of carbon nanofibers, carbon nanobeads, carbon nanoonions and a quantum dot form of carbon. We now know that four basic forms of nanocarbon have been fabricated: fullerene, single-wall carbon nanotube (SWCNT),

multiwall carbon nanotube (MWCNT) and graphene (Figure 2).
In 1991, the U.S. Department of Defense was becoming increasingly interested in using fullerenes and especially carbon fibers for various applications because of their high strength and high Young's modulus, as well as their light weight and high chemical stability. Accordingly, the Department of Defense arranged a conference in the Washington area in 1990 to bring scientists, device engineers, and members of the military together to discuss recent advances in fullerene and carbon fiber research. At one point in the conference, there was a discussion about what fullerenes and carbon fibers (multilayer cylindrical objects now known as multiwall carbon nanotubes; MWCNTs (Figure 2) had in common. This led to the suggestion that if C60 is enlarged to form C70, one can imagine that the enlargement process could continue through C80, C90, C100, and eventually a nanotube with a single wall emerges.

It was Iijima's observation in 1991 of the multiwall carbon nanotubes that heralded the entry of many scientists into the field of carbon nanotubes, stimulated at first by the remarkable 1D dimensional quantum effects predicted for their electronic properties, and subsequently by the promise that the remarkable structure and properties of carbon nanotubes might give rise to some unique applications.

Whereas Iijima's initial experimental observation was for MWNTs, it was less than two years before SWNTs were discovered experimentally by Iijima and his group and by Bethune and his coworkers at the IBM Almaden Research Center (Bethune et.al., 1993). These findings were especially important because the single-wall nanotubes are more fundamental and had been the basis for a large body of theoretical studies and predictions that preceded the experimental.
A major breakthrough occurred in 1996 when Smalley and his coworkers at Rice University (Bethune et.al., 1993) successfully

synthesized bundles of aligned single-wall carbon nanotubes with a small diameter distribution, thereby making it possible to carry out many sensitive experiments relevant to 1D quantum physics, which could not be previously undertaken. Of course, actual carbon nanotubes have finite length, contain defects, and interact with other nanotubes or with the substrate, and these factors often complicate their behavior. A great deal of progress has been made in characterizing carbon nanotubes and in understanding their unique properties since their discovery in 1991.

2.3.3 *Graphene*

Though graphene is the basic form of all nano forms of carbon and even one of the oldest known natural carbon graphite, its existence as graphene, a 2D nanomaterial, became accepted. Graphene is a single layer of carbon packed in a hexagonal (honeycomb) lattice, with a carbon–carbon distance of 0.142 nm. Extensive research on graphene has been done and is being done to develop a method for the creation of single-layer graphene (Sharon, 2010). It has been established that graphene exhibits outstanding structural, electrical, and mechanical properties. Adding to the understanding of graphene has been research focused on phenomena that could be uniquely observed in graphene, like Klein tunneling 2006 (Katsnelson et al., 2006) and the anomalous quantum Hall effect; and, on the other hand, research focused on the similarities and differences in behavior of all the structural, electronic, transport, optical, and thermal properties for monolayer graphene as compared to the various few-layer graphenes with different numbers of layers and layer stacking arrangements.

2.4 Introduction to the Concept of Nano After 1959 and Definitions

The term - **nanometer scale** is due to Richard P. Feynman's great contribution to the field of nanotechnology. One can define the essence of nanotechnology as the ability to work at the molecular level, atom by atom, to create large structures with fundamentally new molecular organization.

The aim is to exploit these properties by gaining control of structures and devices at atomic, molecular, and supramolecular levels and to learn to efficiently manufacture and use these devices.

Nano is the understanding and control of matter at dimensions of roughly 1 to 100 nanometers, where unique phenomena enable novel applications. Encompassing nanoscale science, engineering and technology, nanotechnology involves imaging, measuring, modeling, and manipulating matter at this length scale.

Nanotechnology is the ability to create and manipulate atoms and molecules on the smallest of scales. Nanotechnology can be defined as being concerned with materials and systems whose structures and components exhibit novel and significantly improved physical, chemical and biological properties, phenomena and processes due to their nanoscale size.

Nanoscience is the study of phenomena and manipulation of material at atomic, molecular and macromolecular scales, where properties of the material differ significantly from the properties of material at larger scale.

The term, - **nano,** evolves from the Greek word *nanos*, meaning ‘dwarf’. It is used as a prefix to denote one billionth in a measuring system. So, the particle which has a size of 1 nm is nothing but 1 billionth of a meter by considering the size of the particle. It is generally considered that the modern-day history of nanotechnology started from a speech by Richard Feynman entitled “There's Plenty of Room at the Bottom”.

Nanoscience, nanotechnology and nano engineering: It is the branch of science that deals with the study of fundamental principles and structure of nanomaterials, their properties, and related phenomena known as Nanoscience. It is the interdisciplinary field of science that combines physics, material science, chemistry, and related disciplines. The term nanotechnology was given in 1974 by Norio Taniguchi at an engineering conference in Tokyo (Sataloff, 2018). It is an interdisciplinary branch of science that deals with the design and development of matter at the molecular level. It deals with the collection of methods, techniques, procedures, and skills that produces a nanomaterial. In other words, it studies the application of nanoscience to produce technological devices and products. In 2000, the US government initiated the National Nanotechnology Initiative (NNI) Standards with a vision; a future in which the ability to understand and control matter at the nanoscale leads to a revolution in technology and industry that benefits society (Drexler, 1986).

Nanochemistry is an emerging sub-discipline of the chemical and material sciences that deals with the development of new methods for creating nanoscale materials. The term "nanochemistry" was first used by Ozin in 1992 as 'the uses of chemical synthesis to reproducibly afford nanomaterials from the atom "up", contrary to the nanoengineering and nanophysics approach that operates from the bulk "down". Nanochemistry focuses on solid-state chemistry that emphasizes synthesis of building blocks that are dependent on size, surface, shape, and defect properties, rather than the actual production of matter. Atomic and molecular properties mainly deal with the degrees of freedom of atoms in the periodic table. However, nanochemistry introduced other degrees of freedom that controls material's behaviors by transformation into solution. Nanoscale objects exhibit novel material properties, largely as a consequence of their finite small size. Several chemical modifications on nanometer-scaled structures approve size dependent effects.

2.5 Size phenomenon

With regard to nanoworld, a natural question has arisen - "*where are its boundaries*?*"* Formally, it is restricted by size of nanoparticles, d < 100nm. Physically, it is determined by a variety of size effects. Decrease in size results in the particles physical chemical properties changing and, consequently, the properties of nano-materials are changed dramatically and sometimes cordially. The size effects may be divided into two types, the internal and external ones, as well as the classical and quantum effects. Internal or *intrinsic size effects* are determined as a change of the properties peculiar to particles (the lattice parameters, melting temperature, hardness, band gap, luminescence, diffusion coefficients, chemical activity, sorption, etc.) irrespective of external disturbances.

External size effects arise inevitably and always in the processes of interaction between different physical fields and matters under decreasing of their building units (the particles, grains, domains) down to a crucial value, when this size becomes to be comparable with a length of physical phenomena (the free length of electrons, phonons, coherent length, screening length, irradiative wave length, etc.). In turn, *the classical size effects* appear to become apparent in variation of lattice parameters, hardness, plasticity, thermal conductivity, diffusion, etc. *The quantum size effects* manifest themselves in a blue shift of luminescence, in the rise of peculiar low dimensional quantum states, in the quantization of electroconductivity in magnetic field, in the oscillation of the superconductivity critical temperature, magnetoresistance and other physical characteristics, in the generation of hypersound, etc. Hence, studying the size effects in novel nanostructured materials activated by different external fields, one can hope for the discovery of novel effects and phenomena and for the development of novel nanotechnology on this base.

2.5.1 *The surface of the material*

As the size of the material is reduced to nanoscale, the amount of surface atoms increases resulting in more reactivity of the surface sites. Consider a cube of 1 cm × 1 cm × 1 cm in size. If we cut this cube into equal parts that end with 0.1 mm × 0.1 mm × 0.1 mm, then the total volume of the cube is similar to the original one but the surface of all cubes has 100 times more area than the original. Thus, these materials have a high surface area over volume ratio. If we cut the same cube in the size of 1 nm × 1 nm × 1 nm, then the surface area of the material will increase 10 million times as compared to the original one. This results in an increase in the rate of the chemical reaction as the atoms react more effectively with the surrounding environment. Nanomaterial becomes unstable due to high surface energy. Atoms that exist in the interior are different from the same as compared to atoms that exist on the surface of the material. Hence nanomaterial gets high surface energy due to the dangling bonds at the surface, which results in agglomeration. Many properties like melting point and adhesion are mostly controlled by the surface atoms.

2.5.2 Quantum size effect

When the particle size is reduced to a certain extent (with the particle having a finite number of atoms N), then the electronic energy levels (near the Fermi level of nanometal) change from the Quasicontinuous state into the discrete state. In semiconductor nanoparticles, non-continuous molecular orbitals are occupied at the highest level while the unoccupied are at the lowest level, along with a widening energy gap. When the material properties such as thermal energy, magnetic energy, photon energy, and others are lower than the energy gap spacing, which may result in distinctively different properties than those of the macromolecules. This phenomenon of the widening energy gap is known as the quantum size effect. Thus, Quantum effects play an important role in the determination of the exceptional properties of nanomaterial. Quantum size effects are concerned with the dimension of the materials that can be observed when the size of the particle is too small. These effects are observed due to the change in the atomic structure as a result of the direct influence of ultra-small length on the energy band structure. In the case of bulk material, their properties are determined by the interior atoms as surface atoms in bulk material are negligible. In the case of the nanomaterial, the number of surface atom contributions is maximum. This contribution increases with the decrease in particle size. Thus, the nanomaterial properties are significantly influenced by the surface atoms.

2.6 Classification of Nanomaterial Synthesis Methods

NM synthesis methods can be grouped into three classes in the function of the starting raw materials:
top-down, bottom-up, and hybrid approaches (Figure 3).

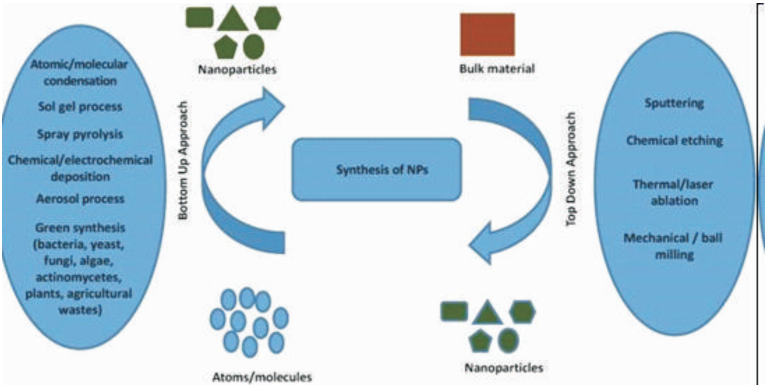

Figure 3: synthesis methods for nanoparticles

2.6.1 *Top-Down Approaches*

Top-down approaches for NM synthesis include mechanical and chemical fabrication techniques. In topdown approaches, NMs are produced by breaking down the bulk material into nanoparticles, typically by attrition, milling, and etching

(Madkour, 2019). Top-down approaches are more suitable for fabricating thin films and NMs larger than 100 nm. These techniques are used for the fabrication of electrical circuits with good integration and connectivity. Integrated circuit fabrication is an example of top-down nanotechnology where tiny mechanical components (e.g., levers, springs, and fluid channels) are embedded in a tiny chip. The main drawback of the current top-down methods is their resolution limit.

2.6.2 *Bottom-Up Approaches*

Compared with top-down methods, bottom-up methods allow for the creation NMs with fewer faults. In such approaches, atoms, molecules, and nanoparticles are the starting material used to create complex nanostructures Isaacoff and Brown, (2017). Ionic and molecularly self-assembly is a bottom-up approach in which chemical or physical forces are used to gather individual blocks/molecules into larger structures through noncovalent bonds, such as hydrogen and ionic bonds, van der Waals forces, and water-mediated hydrogen bonding. Bottom-up approaches allow spatially controlling the properties and composition of the individual blocks. The building block size depends on the desired properties. Wet chemical techniques (e.g., sol-gel, microemulsion) and co-precipitation are bottom-up approaches .

2.6.3 *Hybrid Approaches*

In hybrid approaches, top-down and bottom-up fabrication techniques are combined to develop nanostructured platforms. These hierarchically organized structures are generally difficult or impossible to fabricate using only top-down or bottom-up techniques. Photolithography is an example of a hybrid approach in which etching is the top-down technique, and layer formation (by growth with ions) is the bottom-up method (Marcelo et al., 2020).

2.7 Immeasurable Applications of Nanotechnology aiding technological and industrial revolution The early 2000s saw the beginning of commercial applications of nanotechnology. With thousands of researchers across the globe focusing on the applications of nanomaterials and the mushrooming of many industries, it is now difficult to say who did what first. The realization by scientists and industrialists of the ability of materials to dramatically change their properties at nanoscale has opened up the possibility of making new devices, instruments, consumer goods, etc., to function in a much better way than was possible earlier. Rapid progress in the synthesis and understanding of nanomaterials in just a few years has led to their entry into the world market in a big way. Various fields in which nanomaterials have already entered or are about to enter can be overviewed. The fields in which nanotechnology has contributed immensely are briefly highlighted in Figure 4.

Figure 4: Applications of nanotechnology

2.8 Important Milestones of Nanotechnology in the 21st century

Some important milestones which have led to our understanding of present-day nanoscience and nanotechnology technology and industrial revolution are:

2.8.1 ***Role of nanotechnology behind the success of mRNA vaccines for COVID-19*** Coronavirus disease (COVID-19) was first reported in December 2019, Hubei Province, China. As on

9th December 2021, severe acute respiratory syndrome-coronavirus-2 (SARS-CoV-2) has affected 266018810 people worldwide with 5265092 deaths. The outbreak of COVID-19 pandemic has caused severe public health crisis across the world. Nucleic acids have been emerging as potential drugs to treat a variety of diseases. Lipid nanoparticles (LNPs) have great potential to deliver nucleic acids including mRNAs. Without nanotechnology development of mRNA nano-vaccines for COVID-19 wouldn't be possible.

It is the first time in history that two mRNA-based vaccines developed using lipid nanoparticles (LNPs) have been given emergency use authorization (EUA) by the US FDA for clinical therapeutics against the COVID-19 [Meo, 2021; Khurana et al., 2021)]. This undermines the skepticism on the potential of nanotechnology based approaches. Nanoparticles (NPs) offer many unique advantages compared to other conventional drug carriers including tailored drug release profile, enhanced surface area, protection of the cargo from degradation and modulation of drug pharmacokinetics. Nanotechnology has fast tracked the development of mRNA-based COVID-19 vaccines invented by Moderna and Pfizer/BioNTech . On 16th November 2020, Moderna officially shared the preliminary data of the phase

III clinical trial of its COVID-19 candidate vaccine mRNA-1273 followed by Pfizer- BioNTech on 18th November, 2020 with the clinical trial outcome of its COVID-19 candidate vaccine BNT162b2. Efficacy is an important parameter for vaccines and is defined as the percentage reduction in disease incidence among the vaccinated group during the clinical trial compared with an unvaccinated control group under similar conditions. The primary data revealed BNT162b2 and mRNA- 1273 have an efficacy of 95% and 94.5% against SARS-CoV-2, respectively. The Moderna vaccine is based on a stabilized mRNA of the viral spike protein, and the BNT162b2 is based on a nucleoside modified RNA (modRNA) of the SARS-CoV-2 virus.

The EUA of the Pfizer-BioNTech and Moderna vaccines has undoubtedly brought great hope for the years ahead. However, it remains challenging to decide how to prioritize the allocation of vaccines to the population. While the EUA of these mRNA vaccines brings hope for developed countries, these vaccines remain largely out of reach of developing and underdeveloped nations on economic grounds and need for special storage conditions. At high or at room temperature, mRNA has poor stability, and thus these mRNA-based vaccines need to be stored at such a low temperature. The Pfizer- BioNTech vaccine needs to be stored at - 80 °C to - 60 °C and the Moderna vaccine at - 25 °C to - 15 °C to avoid degradation of mRNA encased inside the LNPs. Further, as it is common to all vaccines, mRNA vaccines are not devoid of side effects, including pain at the site of administration, fever, chills, fatigue, headache, muscle pain, and joint pain. In addition, some patients have experienced allergic responses, which has been linked to the presence of PEG in the formulation (Banerji, 2020)

3.0 MY INNOVATIVE AND INVENTIVE RESEARCH CONTRIBUTIONS

My Vice-chancellor, Sir, since the year 2005, after my Ph.D in nanotechnology-based project, my research has been focused on nanomaterials, nanoparticles, nanobimetallics, nanocomposites, nanohybrids e.t.c which have been taken through basic and applied research to prototypes and technology. I have also taken innovative looks into sustainable nanotechnology with a focus towards circularity for Nigeria in a predictable quality and beneficial environmental consequences.

Lately, and up to this time of my inaugural presentation, I have refocused while widening my research horizon to nanotechnology-enabled forensic sciences, covering anti-counterfeiting and fingerprinting in criminality detection. I am pleased to say that this concept was exported to Regensburg University, Germany between 2017 and 2019. Find below Figure 5 which gives the holistic picture of my research attainment in materials vis-à-vis nanotechnology.

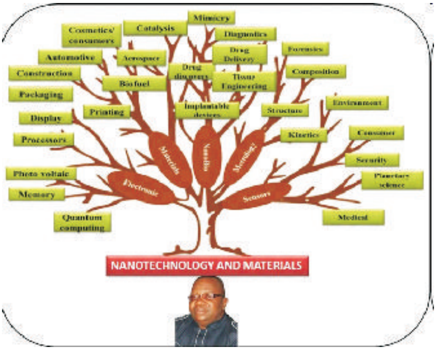

Figure 5: My holistic view research contributions in nanotechnology and materials

3.1 Synthesis of Polyhedral Oligomeric Silsesquioxanes nanomaterials for device applications

Polyhedral oligomeric silsesquioxanes (POSS) represent the new frontier in hybrid materials science and engineering due to their well-defined nano-structure and unique dual nature combining material properties from both inorganic siloxane cage and organic groups at the periphery. These diverse POSS compounds can be introduced into virtually all polymeric systems and generate a myriad of interesting properties including improved mechanical, thermal and surface properties, low dielectric constants, reduced flammability and inflammatory reactions, excellent oxidation resistance and oxygen permeability, to name a few. Thus, POSS has been an important building block for nanomaterials in a wide range of areas such as biomedicine, optoelectronics, coatings, energy, catalysis, aerospace and so on.

Extensive research on POSS as semiconductors, light emitting diodes and other electronic have been done by many companies and universities, including Dow Corning, IBM computer, e.t.c. These materials have been extensively used in semiconductors owing to its tunable periphery functionalities.

With electronic getting smaller and smaller, the need for materials that keep these devices from shortcircuiting is growing in demands. POSS properties have the ability to prevent short-circuiting by acting as rigid and providing durability for devices. However, in-spite of the aforementioned importance of these great materials, its synthetic process and conversion rate leaves much to be desired in which Octavinyl-POSS and H-POSS were obtainable in yield of 7% and 21% respectively before 2006. In the years 2006, we innovatively moved the yields of Octavinyl-POSS and H-POSS to 41% and 72 % respectively by adopting a novel modified synthetic procedure as detailed (Dare *et al*., 2006). Since then, several efforts have been put to create functional materials (e.g. hydraulic lubricant for off-road machines, silicon oxycarbide special glass) from POSS nanocomposites as detailed (Dare 2006; Dare et al., 2004; Dare et al., 2005).

Our recently attempted work on the synthesis of hydridosilsesquioxane using Amberlite cation exchange resin (RSO_3 - H^+, medium porosity IR-120 PLUS) induced us to examine the solid acid or solid base in the hydrolytic polycondensation of some organosilanes, $RSiX_3$ (R = vinyl, phenyl or benzyl; X = Cl, OMe, or OEt). Compound **1** was synthesized by the hydrolytic condensation of $RSiX_3$ in an excess of methanol containing acid Amberlite for hydrolysis. The synthetic procedure adopted, as compared with the literature methods, is shown in Figure 6.

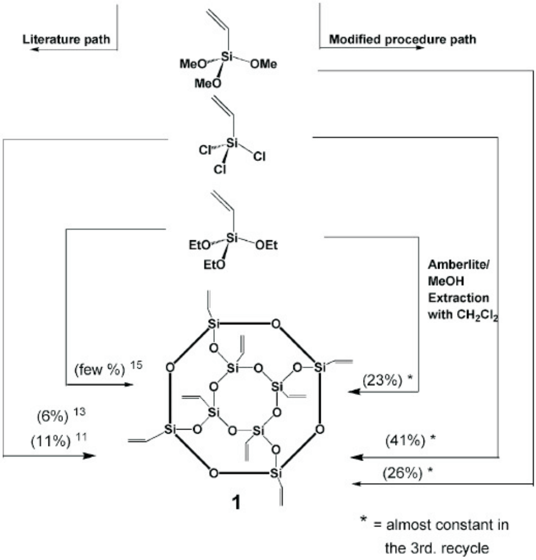

Figure 6: Modified procedure for an improved yield of Vinyl-POSS

Within 13 h of reaction in the presence of vinyltrichlorosilane, there was spontaneous precipitation of **1** from the reaction mixture to give a yield of 23.90% in the first cycle. Repetitive usage of the solid acid was tested by recycling the reactions with the same.

Following reaction equations 3 and 4 (Dare et al., 2006), octabenzylsilsesquioxane was synthesized in ethanol using the solid base Amberlite for hydrolysis. The quantitative product of benzyl-T8 (68%) was obtained after trituration of the resinous semi-liquid. The preparation and regeneration process of the Amberlite ionexchange resin for acid- and base-type are indicated in eqn (3) and (4), respectively.

3.2 Synthesis of POSS and applications for special glasses and lubricating fluids

The complete synthesis of compound **3** was accomplished in a high yield by the reaction of octahydridosilsesquioxane **2** with an excess of 2-chloroethylvinyl ether in the presence of H_2PtCl_6 H_2O as catalyst. The first step involves a sol– gel reaction of $HSiCl_3$ **1** under a water-starved condition by using $FeCl_3$/HCl to give mixtures of silsesquioxanes (i.e., T8 and T10). The mechanism was considered to be hydrolytic polycondensation, which forms the basis for most sol– gel reactions to date. Platinumcatalyzed hydrosilylation of $H_8Si_8O_{12}$ **2** provides a variety of functionalized silsesquioxanes. However, in most cases the products are mixtures of isomers as a consequence of α and β addition to the alkene. For the present study, β addition could be suppressed by using excess of 2-chloroethylvinyl ether such that treatment of **2** with reactant affords a high yield of **3,** which crystallizes spontaneously from solution as colorless crystals. The slow and total evaporation of the mother liquor of **3** in ether solution results in the formation of a single crystal whose Oakridge thermal ellipsoid program (ORTEP) plot is shown in Figure 7. The X-ray crystal structure of **3** reveals that the molecule is required crystallographically to possess a center of symmetry. The linear arms, except that extending from Si3, are virtually all-*trans* in conformation with ω–C—Cl. The arm extending from Si2 has a kind of disorder in the terminal region; the a common feature in the X-ray structure of silsesquioxanes (1.5 nm).

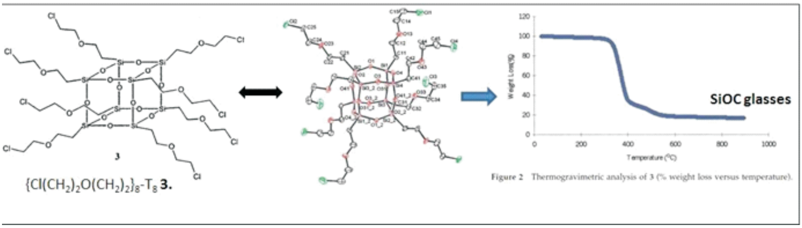

Figure 7: ORTEP plot and thermolysis leading to silicon oxycarbide evolution

Thermal stability of **3** was evaluated thermogravimetrically in air/nitrogen at the rate 10°C/min. **3** is reasonably stable, and experiencing precipitous weight loss above 350°C resulting into silicon oxycarbide glasses. Overall, an inorganic cubic system was converted into a new organic–inorganic hybrid nanomaterial, which hopefully would combine advantageous properties of disparate components into singular silicon oxycarbide glassy nanomaterial (Dare *et al.*, 2004).

Interest in alkyl-functionalized oligoorganylsilsesquioxanes is explained by the determination of the area of practical use such as electrooptics and microelectronics. However, persistence shape, size (0.5-0.7 nm) and high viscosity of some semi-liquid silsesquioxanes have not been taken into consideration as factors that should suggest their potential in some hydraulic applications. Most commercial synthetic hydraulic lubricants are usually formulated from linear organosilicon/silanes having Si-O-Si functionality in their framework, for example, CH_3-$Si(CH_3)_2$-O-$Si(CH_3)_2$-O-$Si(CH_3)_2$-$OSi(CH_3)_3$. The reason behind their adoption is the fact that they are considered high quality base stocks exhibiting unmatched performance, good thermal stability and environmental compatibility.

A report of the synthesis of some new alkylsilsesquioxanes whose alkyl carbon arms are up to $–(CH_2)_8X$ attached at the vertices of the octasilsesquioxane framework by hydrosilylation is presented. In this work, results of the preliminary investigation into the hydraulic lubricating fluid properties of some alkylsilsesquioxanes are also presented (Dare, 2006)

This study was undertaken with 2 objectives in mind: (1) to synthesize some known and new functionalized octasilsesquioxanes, and (2) to take advantage of the viscous nature of some of these products and their Si-O functionality to evaluate their hydraulic fluid properties; the properties were compared with 3 commercially available hydraulic fluids: Mobil EAL 224H (vegetable oil based), Super-V (AP) (petroleum based) and Puroil SHO (synthetic product). Hydrosilylation of octahydridosilsesquioxane **A** using 7-bromo-1-heptene, 8-bromo-1-octene, allyltrichlorosilane and 2methyl-3-butyn-2-ol gave $Si_8O_{12}(CH_2)_7Br$ **B**, $Si_8O_{12}(CH_2)_8Br$ **C**, $Si_8O_{12}(CH_2)_3Si_8Cl_{24}$ **E** and (C-silylated + O-silylated) products **F**, respectively.

These new compounds were obtained in high yields usually in the presence of hexachloroplatinum acid as catalyst and excess of various unsaturated substrates. Toluene was used as solvent during the synthesis of **E** and **F**. **B** and **C** exist as colorless viscous liquids whose kinematic viscosities at 20 ◦C are 47 and 50 cSt, respectively. In a recent report, the carbon chain length of the alkyl substrate placed on the silsesquioxane cores contained up to 6 carbons. Therefore, it was thought that increasing the number of carbons on the alkyl chain to 8 might have an effect on the physical characteristic of the products. The effect on physical property in **B** and **C** can be seen by noting differences in their kv at 20 ◦C. The oil/fluid in a hydraulic system that may be petroleum-based, vegetable-based or synthetic-based (silicon) serves as the power transmission medium, lubricant and coolant. Hydraulic fluids have been rated on their viscosity and anti-wear properties. In this report, the former has been considered on a preliminary scale. Therefore, **B**, **C**, **D** and **H** were evaluated by measuring their kv, Vi and pour point. The Kv at 40 ◦C of **B** (35 cSt), **C** (38 cSt), **D** (cSt)a nd **H** (48 cSt)i s quite reasonable and is higher than that of SuperV, a petroleum-based commercial product (Figure 8). The kv at 100 ◦C of Super-V was the highest among the tested fluids. For most industrial applications, lubricating oils with viscosities ranging from 5 to 15 cSt at 100 ◦C cover the requirements. **H** has a high kv (11 cSt)at 100 ◦C, notably higher than that of Mobil EAL and Puroil SHO, and therefore its utility as a base stock is encouraging.

Its ability to possess good lubricity power even at high temperature is plausibly attributed to the terminal phenyl group on **H**. It has been stated that the presence of a phenyl group in a silicon lubricant10 increases the load-bearing capacity and enhances its stability at high temperature.

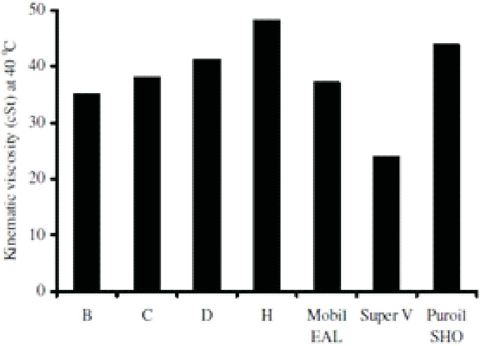

Figure 8: Kinematic viscosity (Kv) at 40°C for POSS lubricants and commercial products

The viscosity index indicates the ability of an oil/fluid to maintain its fluidity or viscosity over a range of temperature. In other words, it is the ratio of the change in viscosity with temperature. The viscosity/temperature graph of the results obtained or **B**, **C**, **D**, and **H** clearly shows that viscosity changes at a very low rate compared to temperature.

The fluid characteristic of silsesquioxanes was determined at low temperature. In a cold-storage study, **B** showed onset of solidification at 0 ◦C, **C** at +8 ◦C, **D** at –5 ◦C and **H** at –20 ◦C. The pour points of **B** and **C** are quite high and this may limit its utilization as a hydraulic base stock. If this property could be enhanced, the scope of its application in hydraulic systems may be widened. No attempt was made to improve the properties of **B** and **C**. The pour points of **D** (-38 ◦C) and **H** (-25 ◦C) are low and fall within the typical range for mineral oils (+6 to –40) even without pour point depressant.

3.3 POSS nanohybrids for dual functional fluorescent and colorimetry fingerprinting detection and anti counterfeiting.

Public security remains a global challenge and the utilization of Latent fingerprint, LFs, bar-codes for anti-counterfeiting, and confidential data encryption, among others, are being currently applied by forensic institutions. In particular, LFs appears to be the best option for personnel identification in forensic investigations due to their high stability, uniqueness and complexity of ridges patterns. In an attempt to improve the traditional fingerprint detection methods, fluorescent nanomaterials have been found to be suitable platforms for the development of LFs. Among co-doping of 2D nanostructures, a rigid 3D hetero-structural scaffold could be a promising candidate due to its efficiency, photostability and effectivity.

Counterfeiting of valuable documents, currency and branded products is a challenging problem that has serious economic, security and health consequence for governments, businesses and consumers all over the world. It is estimated that counterfeiting represents a multi-billion dollar underground economy with counterfeit products being produced on a large scale every year. Counterfeiting is an increasingly hightech crime and calls for high-tech solutions to prevent and deter the acts of counterfeiting.

In this regard, polyhedral oligomeric silsesquioxanes (POSS) have emerged as a valuable group of 3D nano-building-blocks for the fabrication of a variety of hybrid functional materials. Several prime qualifications make POSS the appropriate choice for its use as principal core: (i) it exhibits high stability and excellent biocompatibility in a biological environment, (ii) the inorganic cage provides not only protection to the covalently attached dye from stability but also a convenient framework for 3D multivalent display of pendant epitopes, (iii) facile functionalization.

Dare *et al*., (2020, 2021), developed novel FLMs based on the 3D POSS containing fluorescent dyes for LF visualization materials. The synthetic strategy has followed the classical "click" reaction where the CuI-catalyzed [3+2] cycloaddition between the POSS precursor with an azide group (Fig. 9) and the corresponding alkyne-like fluorophore has been carried out. It is worth mentioning that the use of "click" chemistry has been proved to be a versatile tool for preparing a large variety of POSS conjugates for different applications, including POSS-dye derivatives. Herein, four different materials relying on the fluorophore nature (pyrene=PAP; dansyl=PAD; bromo-naphthalic anhydride=PANA; piperazinenaphthalic=PANP) have been obtained. Their photophysical properties, as well as measurements on the photostability of these species have been investigated in detail and, finally, these FMLs have been successfully tested for the detection of LFs.

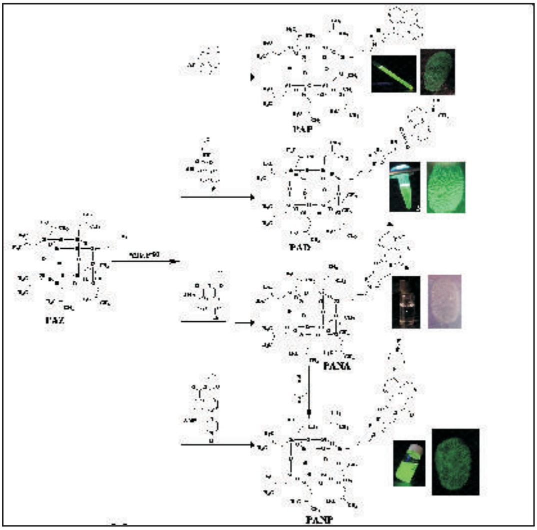

Figure 9: Synthetic procedure for PAP, PAD, PANA and PANP, with inset indicating their corresponding UV lamp (365 nm) irradiation and fingerprint response.

Some conclusions were drawn from the photophysical data: large Stoke's shift were obtained in general, high fluorescence quantum yields were observed in some cases and an ideal photostability made these FLMs (PAP, PAD and PANP) potential candidates to be successfully applied as fluorescence-based fingerprinting detection materials.

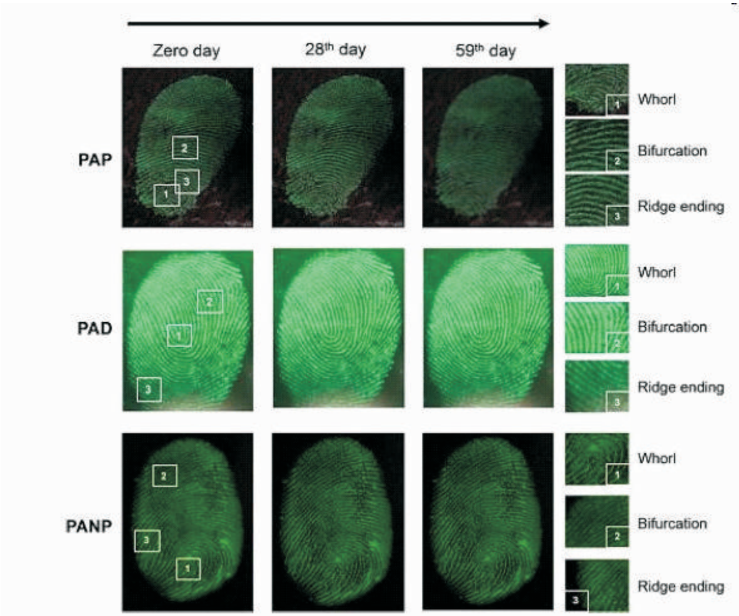

Figure 10. Photographs of fingerprints on smooth plastic surfaces detected by means of PAP, PAD and PANP. Enlarged areas marked with numbers are given on the right.

Figure 10 displays fresh (0 days) and aged fingerprint images (stored at RT for 28 or 59 days). The undeveloped fingerprint patterns were hardly visible regardless the illumination (UV or vis light). In contrast, those developed under diluted solution of the FLMs apparently displayed enhanced legibility due to the greater contrast between the fluorescent ridge and non-fluorescent furrow. The brightness, contrast and visual legibility remained the same for at least three months for PAD and PANP. However, dimmer fingerprint fluorescence was observed with PAP after one month, probably due to loss of some components on the ridges over time. The longer temporal stability observed for PAD and PANP was ascribed to their respective structural outfit bearing functional groups capable of providing hydrogenbonding with the residual amino acids in the fingerprints (e.g. (PAD)S=O···H@N (amino acid), (PANP)N@H···O(amino acid)). In addition, N atoms also contribute forming strong N···H@O interactions. Furthermore, detailed observation of the friction ridge features (see enlarged areas in Figure 11), showed whorl, bifurcation, and ridge ending, which satisfy to a large extend the requirements of fingerprint identification.

Interestingly, our fingerprint development process also offered distinguished visual legibility on other surfaces, including handset phone surfaces. In fact, PAP, PAD and PANP were successfully used to visualize latent fingerprints on several surfaces, providing reasonable legibility pattern that satisfy the needs of fingerprinting identifications in forensic technology (Dare *et al*., 2021)

We have also developed highly efficient latent fingerprint detection by eight-dansyl-functionalized octasilsesquioxane nanohybrids (Dare et al, 2021). The 3D **POSS** nanohybrids were synthesized following a three-step procedure.

These nanohybrids were fully characterized and the photophysical study revealed significantly higher molar absorption coefficient for **POSS-D8**, while the fluorescence quantum yield was 2 times higher in the case of **POSS-S-D8**. Both FLMs displayed exceptionally distinguished photostability well above that of the *N*-dansyl propynyl precursor. The two photoresponsive octadansyl labeled POSS enabled the detection of latent fingerprints on phone glassy surfaces with very good legibility according to the requirements for forensic applications.

3.4 Dual−mode colorimetric/fluorescent fingerprint imaging based on rhodamine ethylenediamine bis(triazolyl POSS)

Inspired by our most recent work, Dare *et al*, (2020, 2021) where we successfully took advantage of fluorophore-triazolyl-POSS for fingerprint imaging, coupled with various reported M^+ -X complexes , we considered it worthwhile to adopt the fluorescent and colorimetric attributes of **RBS–M**$^{2+}$ in fingerprint imaging. For these studies, fingerprints of selected donors were imaged and detected via both fluorescent and colorimetric responses of **RBS–Cu**$^{2+}$ and **RBS–Zn**$^{2+}$ with high sensitivity, selectivity and legibility (Fig. 11).

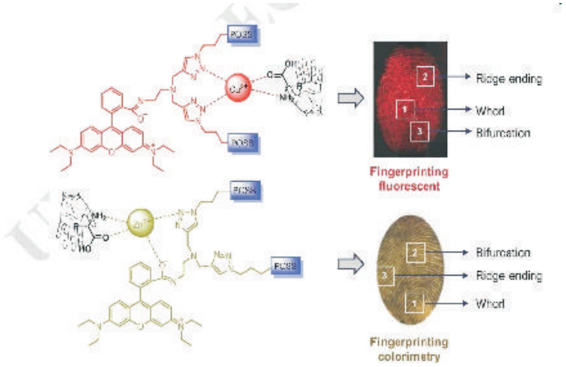

Figure 11: Proposed mechanism of fingerprint formation based on [**RBS-M**$^{2+}$]–finger amino acid interactions

Detailed observation of the ridge features showed Whorf, bifurcation and ridge ending which to a large extent fulfill the requirements of fingerprint identifications in forensic science.

A judicious balance of hydrophobic and π–π interactions have been recognized in previous reports. Accordingly, **RBS–M**$^{2+}$ was designed to possess multiple binding profiles which are subsequently available for interaction with the –C=O and $–NH_2$ of amino acids in fingerprint oils (Fig. 11). The whole ensemble, which consists of **RBS–M**$^{2+}$ in non-covalent interactions with

–C=O and $–NH_2$, formed a ternary complex that cooperatively work to provide stabilized fingerprint detection and eventual imaging. Some fluorescent chemosensor systems have been developed to detect amino acids based on probe–metal ion ensembles. Importantly, brightness, contrast and visual legibility remained unchanged up to 1 year, when developed with **RBS–Cu^{2+}** under fluorescent response (2 equiv of Cu^{2+}).

3.5 Fluorescent labeled POSS for anti-counterfeiting

Our novel Dansy labeled POSS (DLP) and pyrene labeled POSS (PLP) have been explored for anticounterfeiting purposes in the form of covert signals and “Quick Response” (QR) bar codes with the view to detect various fraudulence practices on Nigeria Naira notes, CD disk and potentially faked materials in the circulation which has brought socio-economic woes to the whole world.

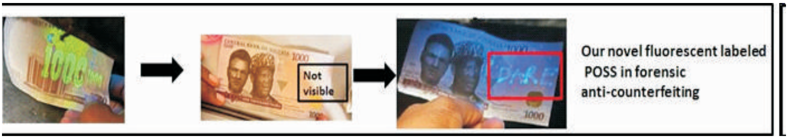

Figure 12: Covert Anti-counterfeiting on N1000 note

After formulation of DLP or PLP in appropriate solvent system, inscription in my name was applied on N1000 naira note COVERTLY for subsequent UV lamp illumination and signal detection. The originally invisible (COVERT) marked portion bearing my name became visible under 365 nm UV lamp illumination (Figure 12). This inscription remains stable with no traces of photodegradation for good one year. The anti-counterfeiting profile displayed by DLP and PLP developed by us is adequately comparable to the fluorescent 1000 put on the note by Central Bank of Nigeria. Indeed, there is no need for CBN spending huge resources to the external world for anti-counterfeiting.

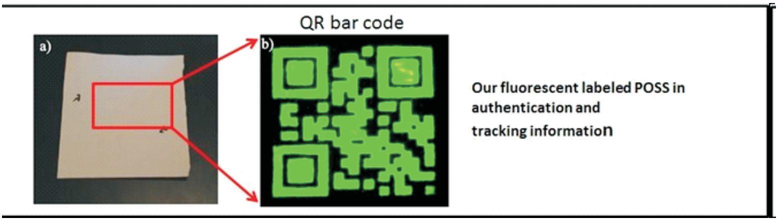

Figure 13: QR bar code tracking and anti-counterfeiting

Datas were accessed by scanning the QR code with the camera built into a smart phone and processing the image with a QR code scanner application. These matrix bar codes have rapidly gained international popularity and are now very commonly used in various products, because of fast readability and large storage capacity. QR codes are typically used for authentication and tracking information, but not in security applications.

While adopting the same DLP and PLP formulations and made inscriptions on papers in printing mode, we demonstrated that the printing of QR codes which are invisible on paper and transparent tape, could produce fluorescent images under UV lamp (365 nm) excitation which can be read and decoded with an unmodified smart phone (Figure 13).

3.6 Dual‒mode colorimetric/fluorescent Chemical Sensor (Chemosensor) based on rhodamine ethylenediamine bis(triazolyl POSS)

The design and synthesis of novel nanoscopic molecules that can recognize and detect cations and show specificity for biologically relevant metal ions have gained attention during the last decade. Particularly, Cu^{2+}, Zn^{2+} and Fe^{3+} play vital roles in several biological, environmental and chemical systems. These metal ions are essential trace elements for both plants and animals, including humans. Literature medical data reiterates that excess accumulation of Zn^{2+} has the propensity to alter Cu^{2+} and Fe^{2+}/ Fe^{3+} absorption in humans and eventually lead to a series of health

problem.
While several expensive and time-consuming spectroscopic analytical techniques could detect and discriminate Zn^{2+}, Cu^{2+} and Fe^{2+}/ Fe^{3+} among many other metals, a more accurate and sensitive probe would be beneficial for detecting these biologically relevant cations.

Novel rhodamine bis(ethylenediamine triazolyl POSS), (i.e., **RBS**), was obtained in 82% yield by CuAAC reaction between **PA** and **RED**. 1H NMR spectra and many other spectroscopic techniques confirmed the structure of **RBS** with evidence of bis(triazole) protons, an indication of a successful CLICK chemistry.

We explored its photophysical properties in different solvents which included absorption/emission bands, molar absorption coefficients, Stokes shifts, fluorescent quantum yields, emission rate constants, singlet energies and lifetimes. With the photophysical data in hands, **RBS** might be a potential candidate to be successfully applied as an "OFF-ON" metal sensor, since the possible coordination could evade formation of the aggregates and enhance the radiative pathways.

To establish the sensing capacity of RBS, we first evaluated its photophysical properties, focusing mainly on the emission property changes due to the low sensitivity that UV–visible (absorbance) measurements usually exhibit. Upon separate addition of several metal ion solutions to **RBS**, only Cu^{2+} and Zn^{2+} exhibited a strong fluorescent band (580 nm) with Cu^{2+} having stronger emission band (Fig. 14).

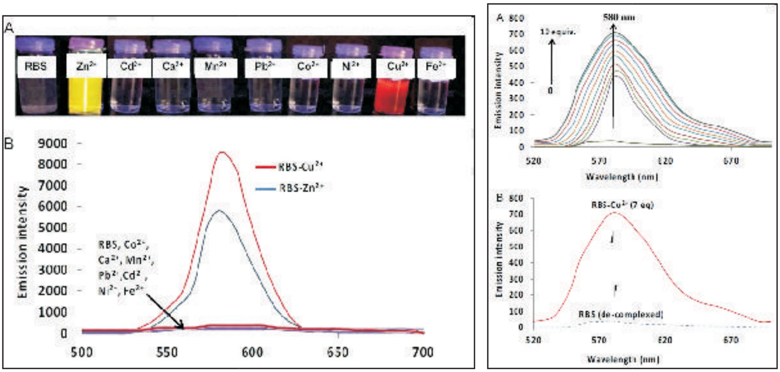

Figure 14: **A** Photographic images and fluorescent responses of **RBS** (20 µM) in the presence of various metal ions. **B** Fluorescent changes of **RBS** upon addition of various metal ions (10 µM)

This observation indicates that only Cu^{2+} and Zn^{2+} from among the tested metal ions could coordinately chelate with **RBS** and, eventually, emit reddish pink and yellowish green fluorescence, respectively. **RBS–Cu^{2+}** and **RBS–Zn^{2+}** with enhanced fluorescent profiles corroborated with a 63.3-fold (0.41) and 48.3-fold (0.29) enhanced quantum yield when compared with the highest achieved by **RBS** in MeCN. These results provide a platform for Cu^{2+} and Zn^{2+} sensing in either biological or environmental condition accompanied by structural transformation occasioned by ring opening of the spirocyclic unit via a - “turn-on” chelation-enhanced fluorescent (**CHEF**) mechanism. It is worth mentioning that we also tested additional monovalent and trivalent ions (i.e., $Al^{3+,}$ Fe^{3+}, Cr^{3+}, Na^{+}, Ag^{+} and K^{+}). However, titration experiments resulted in non-coordinated uncomplexed colloidal suspensions, which made further photophysical experiments rather difficult. Therefore, we limited in this study the probe responses to representative divalent metal ions shown in Fig. 14A.

The reversibility of, in particular, **RBS–Cu^{2+}** formation is underscored by a reversible color transition from reddish pink back to colorless upon addition of EDTA which brought down the emission intensity to the same level as in the original uncomplexed **RBS** (Fig. 14B). Thereby, the loss of the spectroscopic features of the system due to the induced decomplexation process would be indicative of the restoring of the spirocyclic form. The equilibrium interchange between the open and closed spirolactam ring in reversible motif prompted by EDTA addition could be an index for monitoring metal complex formation and subsequent sensing of $M^{2+.}$Fluorescent transition from colorless to reddish pink and colorless to yellowish green favoring **RBS-Cu**$^{2+}$ and **RBS–Zn**$^{2+}$ falls within the addition of 1–7 equiv of metal ions to **RBS**. From Benesi– Hildebrand plots, we could determine the binding constants of 5.12×10^{8} and 3.6×10^{8}, respectively, which are high enough to justify stable **RBS–M**$^{2+}$ bindings. The detection limit of Cu^{2+} and Zn^{2+} via fluorescent response was the same as 3.0 nM, which allows sensing of both metal ions in the nanomolar concentration range.

It is noteworthy that colorimetric responses capable of being detected with the naked eye proceeded with the incremental addition of metal ions (8–10 equiv) to **RBS** (Fig. 15A). The colorimetry responses were supported by a linear relationship between the absorption intensity at 452 nm and various concentration of metal ions in the range 1–100 µM (Fig. 15B) with correlation coefficients of 0.9926 (**RBS–Cu**$^{2+}$) and 0.9923 (**RBS–Zn**$^{2+}$). The limit of colorimetric detections of **RBS** for **Cu**$^{2+}$ and **Zn**$^{2+}$ were 2.14×10^{-8} and 4.0×10^{-8} mol L^{-1}, respectively. Hence, the results (Dare *et al.*, 2023) obtained, to a large extent, validate the reliability and practicality of the established dual-mode colorimetry and fluorescent sensing of Cu^{2+} and Zn^{2+}.

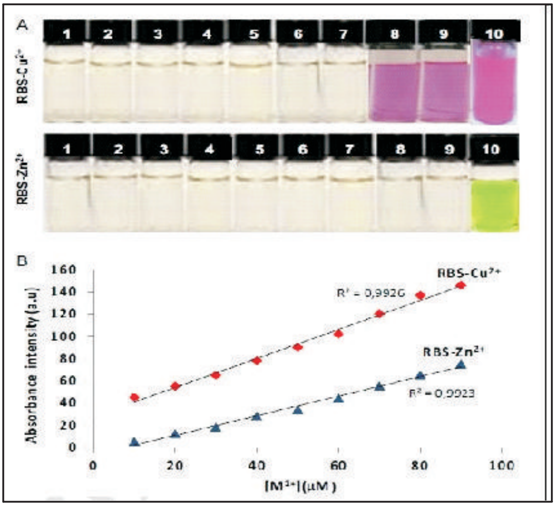

Fig. 15 **A** RBS colorimetric response during detection of Cu^{2+} and Zn^{2+} at different metal concentrations (from left to right: 1–10 equiv). **B** A linear relationship between absorbance intensity at 468 nm and concentrations of M^{2+}(Cu^{2+} and Zn^{2+}).

The observed dual-mode visuality prompted by fluorescent and colorimetric responses of **RBS** to Cu^{2+} and Zn^{2+} occasioned, undoubtedly, the plausible binding modes vis-à-vis structural orientation as detailed. Job's plot indicates that **RBS–Cu^{2+}** and **RBS–Zn^{2+}** have preferences for 2:1 and 1:1 binding stoichiometry, respectively. The observed discrepancy in the binding stoichiometry suggests different binding orientations with respect to bistirazole (–N=N–Cu–N=N–) and open spirolactam carbonyl of the amide/triazole (O–Cu–N=N). Plausibly, once the Cu^{2+} or Zn^{2+} is fixed in the cavity of **RBS** via the coordination– bonding interaction, the electron cloud on the electron rich imine fragment will transfer to the large rhodamine ring system resulting in the ring opening of spirolactam amide to form a fivemember or six-member ring. The exclusive sensing of

Cu^{2+} and Zn^{2+} owes to the stronger ability of these ions toward the ligand due to the optimal size of **RBS** cavity.

3.7 Metal nanoparticles, metal oxide nanoparticles, nanobimetallics and nanocomposites for various applications

As an independent researcher flanked by several mentees whose Masters or Doctoral degrees was majorly supervised by me, I have been actively involved in the synthesis, characterization, properties and applications of silver nanoparticles (AgNPs), gold nanoparticles (AuNPs), palladium nanoparticles (PdNPs), cobalts nanoparticles, platinum nanoparticles and their allied which include, but not limited to Ag-Co, Ag-Ni, Ag-Pd, Ag-Pt, Ag-Chitosan, Ag-ZnO, Ag-Au, Ag-SiO_2, Ag-$CoPO_4$, Au-Pd, Au-Pt, e.t.c. Metal oxide nanoparticles and allied in their core-shell, alloy and bimetallics with applications in catalysis, Hg sensor, humidity sensor, antimicrobial activities were also studied (Figure 16). These nanoparticles and hybrids have resulted into diverse morphologies (nanosphere, nanorods, nanowires, nanoflakes, nanodisks, nanocubes e.t.c). My contributions in these areas of nanostructured using chemical and green nanotechnology approaches have resulted in over 40 significant publications including 2 books. My contributions are partly highlighted in Table 1 indicating metal and metal oxide nanoparticles and hybrids, synthetic methods, morphology, properties and applications

Table 1: Collations of synthesized metals, bimetallics, metal oxides hybrids nanoparticles using chemical and green approaches exhibiting various properties and applications

Metal and metal oxide nanoparticles applications	Synthetic method	Morphology and sizes (nm)	Properties and	Mentee(s) involved and hybrids	Remark
Silver nanoparticle (AgNPs)					
AgNP	Chemical	Core-Shell, nanorod (12.2)	Antimicrobial	-	Dare *et al*, 2012
AgNP	Chemical	nanorod (42.6)	Optical	Dr. J. Adekoya	Adekoya & Dare 2014
AgNP	Chemical	nanodisc (11.23)	Optical	Dr. J. Adekoya	Dare & Adekoya 2015
AgNP	Green	Spherical (12.4)	Antibacterial	-	Dare *et al*, 2015
AgNP	Green	Spherical/Twinned (8 -53)	Growth kinetic	-	Dare *et al*, 2015
AgNP	Green	Spherical (10.2)	Electro-oxidation	Dr. K. Sodehinde	Dare & Sodehinde 2016
AgNP	Green	Spherical (16-25)	Optical	Dr. K. Sodehinde	Dare & Sodehinde 2016
AgNP	Green	Spherical (16.2)	Optical	Dr. A. Labulo	Dare & Labulo 2016
AgNP	Green	Spherical (17.05)	Sensor	Dr. A. Labulo	Dare & Labulo 2016
AgNP	Green	Spherical (13.8)	Optical	Dr. K. Sodehinde	Dare & Sodehinde
2016					
AgNP	Green	Nanocluster (NA)	Optical	Dr.Mrs.B.Akinsiku	Dare & Akinsiku 2016
AgNP	Green	Spherical (27.81)	Optical	Dr.Mrs.B.Akinsiku	Dare & Akinsiku 2018
AgNP and allied (Ag-X)					
Ag-ZnO	Chemical	Nanorod (11-56)	Humidity sensor	Mrs.B.Adanu	Dare and Adanu 2023
Ag-Pt	Chemical	Nanocube alloy (30.55)	Catalysis	Dr. J. Adekoya	Dare & Adekoya 2014
Ag-Ni	Chemical	Core-Shell (14.46)	Optical	Dr. J. Adekoya	Dare & Adekoya 2014
Ag-Pd	Chemical	Spherical alloy (31.5)	Catalysis	Dr. J. Adekoya	Dare & Adekoya 2014
Ag-X,X	Chemical	Core-Shell (10.3)	Fluxional	Dr. J. Adekoya	Dare & Adekoya 2015
Ag-Ru	Chemical	Core-Shell (18.89)	Optical	Dr. J. Adekoya	Dare & Adekoya 2015
Ag-Co	Chemical	Spherical (16.51)	Optical	Dr. J. Adekoya	Dare & Adekoya 2015
Ag-Ni	Green	Core-Shell (18.64)	Optical	Dr.Mrs.B.Akinsiku	Dare & Akinsiku 2018
Ag-Ni	Green	Data based	Antimicrobial	Dr.Mrs.B.Akinsiku	Dare & Akinsiku 2018
Ag-Co	Green	Core-Shell (391)	Antimicrobial	Dr.Mrs.B.Akinsiku	Dare & Akinsiku 2019
Ag-Ni	Green	Quasi nanocube (19.14)	Antimicrobial	Dr.Mrs.B.Akinsiku	Dare & Akinsiku 2020
Ag-$CoPO_4$	Green	Quasi nanocube (31.94)	Antimicrobial	Dr.Mrs.B.Akinsiku	Dare & Akinsiku 2020
Ag-Co	Green	Spherical (10.5)	Sensor	Dr. F. Oladoyinbo	Oladoyinbo & Dare 2018
Ag-Chitosan	Chemical	Film	*In-viro* release	Dr. I.Sonde	Dare & Sonde 2016
Ag-Chitosan	Chemical	Film	*In-viro* release	Mrs. Olaniyan/Shephra	Dare & coworkers 2016
Gold nanoparticle (AuNP)					
AuNp	Green	Spherical (12.6)	Sensor	Dr.K . Sodehinde	Dare & Sodehinde 2018
AuNp	Green	Spherical (19.7)	Sensor	Dr.K . Sodehinde	Dare & Sodehinde 2016
AuNp	Green	Spherical (20-25)	Optical	Dr.K. Sodehinde	Dare & Sodehinde 2016
M = Co, Ni, Ru, Pd, Pt	Chemical	several morphologies	Optical	Dr. J. Adekoya	Dare and Adekoya 2015
Zinc nanoparticle and its allied					
ZnO-Se/graphite	Chemical	Agglomerates	Photodegradation	Dr. I.Sonde	Dare & Sonde 2017
ZnO-dye	Chemical	Twinned (8.3)	Solar cell	Mr.D.Bada, Dr. W. Ayinde Dr. S. Alayande	Dare & coworkers 2017

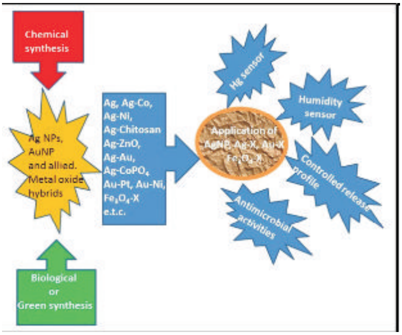

Figure 16: Applications of AgNPs, Ag-X, Ag-metal oxide synthesized by chemical and green means

It is of note that physical and chemical methods of producing nanoparticles and nanomaterials involve the use of toxic chemicals, and these protocols pose a threat to the environment and human health.

Moreover, the procedures are costly while the products are hardly appropriated for medicine. Hence, the application of green chemistry in nanotechnology is considered an alternative to overcome earlier mentioned problems.

Microorganisms, plants, and plant extracts are often utilized in place of chemicals for the biosynthesis of nanoparticles and nanomaterials. Furthermore, plant-mediated synthesis is of many advantages, like sustainability and renewability of plant materials, which are the sources of secondary metabolites – the reducer. The protocol is also nature-friendly, cost-effective, rapid, etc. Metal ion reduction is possible by plant extracts due to the presence of chemicals and bioactive compounds (phytochemicals) naturally present in them, most notably the medicinal plants, has been identified to contain phenolic compounds, terpenoids, essential oils, and alkaloids, which includes an *N*-methyl group. These active functional groups in plants it as a metal ion reducer for the formation of nanoparticles.

In a brief, aside our several novel protocols presented for the chemical synthesis of monometallic AgNPs, (Dare and Adekoya, 2014, 2015; Dare *et al.*, 2012), we have successfully synthesized monometal NPs by a direct and efficient wet chemical method via exclusive reduction of $M^{2+}/M^{3+}/M^{4+}$ (M = Co, Ni, Ru, Pd, Pt, Ru) by polyol, hydrazine monohydrate or sodium borohydride in the presence of poly(vinylpyrrolidone), trisodium citrate and dodecanethiol organic matrices. The resulting monometallic nanoparticles were found to be easily dispersible in aqueous or organic solvent. There were high indexed faceted structures formed as a result of thermodynamic controlled hydrolysis and condensation processes leading to slow particle growth with resultant size confinement (Dare and Adekoya, 2015). The UV/visible absorption spectra of Co, Ni, Pd, Pt monometallic sols stabilized by PVP/GLY at 175 °C, 2 h and Ru sols at 200 °C, 2 h respectively with different metal precursors/ligand mole ratios as shown in Table 2. The optimum stoichiometric ratios for the precipitation reactions which produced the PVP/polyol capped monometallic sols with different metal stabilizing agent mixtures are 1.01:0.05, 1.02:0.04, 0.34:0.02 and 0.10:0.03 for Co/PVP/GLY, Ni/PVP/GLY, Pd/PVP/GLY and Pt/PVP/GLY respectively. At these ratios, colloidal dispersions were formed which were easily redispersed in ethanol and the optical absorption of metal sols was conveniently measured.

In the global efforts to reduce generated hazardous waste, “green" chemistry and chemical processes are progressively integrating with modern developments in science and industry. Various approaches using plant extracts have been used for the synthesis of silver nanoparticles. These approaches have many advantages over chemical, physical, and microbial synthesis because there is no need of the elaborated process of culturing and maintaining the cell, using hazardous chemicals, high-energy and wasteful purifications.

In an attempt to widen the scope of naturally, environmentally benign and easily available bioresourceable greens for the synthesis of metal nanoparticles, Dare *et al*. (2015) have screened biodiversified plant extracts and looked into their capability for the synthesis of AgNps (Table 1). Most of the plant-mediated bioreductions in this work are being studied for the first time. It is noteworthy that, with the aid of UV–Vis spectroscopy as time-resolved monitoring device, a number of the extract demonstrated unprecedented fast bioreduction reaction onset activity promptly within the first 2 min accompanied with fast reaction rate. There were cases of red shift in the observed PBR wavelengths as indication of cappings from organics inherent in the bioextracts. Furthermore, we have engaged the combination of both TEM and time-resolved UV–Vis to monitor and predict the growth kinetic mechanism of AgNPs synthesized from biodiversified plant extracts. The experimental data were analysed within the framework of the existing coarsening and particle growth mechanism, i.e. OR and OA. Based on the prior timescale analysis of the individual events, we proposed for some plant extracts' (Ao, Pg, Nl, Gl, Pig and Xa) bioreduction a single-stage time-sequenced description which follows nucleation of AgNPs and its growth by diffusion control that complies with OR by virtue of linearity experience in a r3 versus time plot. However, a two-stage growth mechanism has been proposed for another set of plant extract (Am, Og, Cc and Va)-mediated synthesis which involves (1) an intermediate transition diffusion controlled via OR and finally surface adsorption of organic passivating agent by OA. In this case, coarsening and assembly processes are likely.

Indeed, this is the first preliminary demonstration through green experimental protocol of the ability to predict the coarsening of silver nanostructure evolution via OR or OA. In principle, the proposed mechanistic framework, hopefully, provides underlying guides for tracking other nanostructure evolution in a green environment. Several other green nanotechnology approaches for the synthesis of monometallic and bimetallics nanoparticles have been developed by Dare and Akinsiku (2016, 2018); Dare and Sodehinde (2016, 2016), Dare and Labulo (2016) and Dare and Sodehinde (2018) (Table 1)

3.7.1 *Catalysis:*

Dare and Adekoya (2014) reported synthesis of polyol based Ag/Pd nanocomposites for applications in catalysis. The synthesis of polyvinylpyrrolidone seed mediated Ag/Pd allied nanobimetallic particles was successfully carried out by the simultaneous reduction of the metal ions in ethylene glycol, diethylene glycol, glycerol, pentaerythritol and sodium borohydride solution. The optical measurement revealed the existence of peak broadening that causes diffusion processes of the metal sols to decrease making it possible to monitor the changes spectrophotometrically. This, together with X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM) and high resolution TEM measurements strongly support the conclusion that intimately alloyed clusters were formed and the particle growth anisotropy is diffusion limited. This was observed for the Ag/Pd nanoparticles passivated with PVP/GLY which confirms the alloy formation whereby the Ag metals appear as dark spots while Pd metals are seen as the brighter conjugates measuring 15.05 ± 4.68 and 5.37 ± 1.53 nm, respectively. The rapid catalytic conversion of 4-nitrophenol to 4-aminophenol after addition of Ag allied nanobimetallic particles Ag/Pd was quantitatively monitored as a successive decrease in the peak height at 400 nm and the gradual development of new peak at 300 nm which confirmed the formation of 4-aminophenol by a corresponding change in colour of the solution from light yellow to yellow-green. In this experiment, the concentration of the borohydride ion, used as reductant, largely exceeded that of 4-nitrophenol. As soon as freshly prepared $NaBH_4$ solution was added, the Ag/Pd nanoparticles started the catalytic reduction by relaying electrons from the donor to the acceptor 4-nitrophenol after the adsorption of both onto the particle surfaces. As the initial concentration of sodium borohydride was very high, it remained essentially constant throughout the reaction. For the evaluation of catalytic rate, it was reasonable to assume the pseudo-first-order kinetics with respect to 4nitrophenol.

In a similar vein, Dare and Adekoya (2014) developed tunable morphological properties of silver enriched platinum allied nanoparticles and their catalysed reduction of p-nitrophenol. A robust polymer based and polyol mediated procedure to synthesize nanobimetallic particles has been modified to produce core–shell and alloy Ag/Pt nanoparticles with tunable properties.

Novel three-dimensional (3D) quasi nanocubes entangled in nanowebs were produced by rapid solution phase transformation with hot addition of absolute ethanol. The optical characterization showed extinction of plasmon resonance band occurring with incremental feeding ratio of Pt source in all cases. Transmission electron microscope (TEM) and high resolution transmission electron microscope (HRTEM) images revealed that the shape, size and size distribution of as-prepared silver platinum nanoparticles depended on the stabilizer or capping agent, mole ratio of metal ion sources, temperature and time of reaction. Meanwhile, catalytic activity was highest in the reduction of p-nitrophenol in the presence of polyvinylpyrrolidone/diethylene glycol stabilized Ag/Pt nanoparticles. The nanocube measured 30.45 ± 6.23 nm which is evidently 3D quantized. Looking at the catalytic reduction of 4nitrophenol at 299 K, Ag/Pt/ PVPCOH nanocatalysts investigated, they exhibited relatively higher rate constant than monometallic Ag nanoparticles, showing the significant input of new nanocomposite material.

3.7.2 *Heavy metal ion and humidity sensors*

The design and synthesis of novel nanoscopic molecules that can recognize and detect cations and show specificity for biologically relevant metal ions have gained attention during the last decade. Particularly, Cu^{2+}, Zn^{2+} and Fe^{3+} play vital roles in several biological, environmental and chemical systems. These metal ions are essential trace elements for both plants and animals, including humans. Literature medical data reiterates that excess accumulation of Zn^{2+} has the propensity to alter Cu^{2+} and Fe^{2+}/ Fe^{3+} absorption in humans and eventually lead to a series of health problem.

In this view, Dare and Labulo (2016) have developed green nanotechnology protocol and probe based on capped AgNPs for the colorimetry sensing of dangerously toxic mercury ion (Hg^{2+}) and heavy Iron III (Fe^{3+}). The colorimetric sensing property of DAgNPs was assessed by its color change after the addition of metal ion. The brownish-red AgNP solution was able to selectively recognize Hg^{2+} by disappearance of the typical brownish-red color to form a colorless solution while other metal ions did not give distinct color change except Fe^{3+}. The absorption spectra showed the disappearance of SPR at 430nm. LOQ values of 2.11 µmg mL^{-1} and 15.21 µmg mL^{-1} were recorded for the Capped-AgNPs sensing of Hg^{2+} and Fe^{3+} respectively. Summarily, the values obtained for the LOD, LOQ and Sandell's sensitivity indicate that capped AgNPs can serve as highly sensitive colorimetric sensor for toxic and heavy metal Hg^{2+} and Fe^{3+} respectively.

Metal nanoparticles (MNPs)-based electro-analytical technique shows the enormous potentials for constructing enhanced platforms for chemical sensing and biosensing. MNPs-based colorimetric methods (which utilizes, the changes in the Surface Plasmon Resonance (SPR) bands of Au or Ag NPs) are extremely attractive due to their simplicity, high sensitivity, low-cost, easily readable with the naked eye, and allow onsite, real-time qualitative or semi-quantitative detection without complicated analytical instruments. However, in the presence of AgNPs, Dare and Sodehinde (2016, 2018) developed a rapid, simple and green method for sensing mercury (II) ions in aqueous solutions based on the shift in the localized surface plasmon resonance of biosynthesized gold nanoparticles (Au NPs) using *Chrysophyllum albidum* aqueous extract. From the kinetic studies, the first-order rate constant value of 8.89×10^{-5} s^{-1} is obtained. Red shift in surface plasmon band of Au NPs from 520–540 nm to around 650 nm in a concentration-dependent manner is observed in the presence of

Hg^{2+} ions. The limit of detection and percentage recovery are 0.001 mg/L and 89–93%, respectively. Sensing capacity of the method is successfully applied to Iju river water samples. This novel method shows excellent sensitivity and selectivity for Hg^{2+}, and it can be applied to the determination of Hg^{2+} in water samples.

Humidity measurement problems and control are some of the most significant issues in various areas of applications such as, agriculture, automated systems, instrumentation, and climatology. Humidity is the amount of water vapor present in the air, and it plays a vital role in every part of the earth's biological and automated processes. Humidity is highly variable and changes according to season, land and sea, among others. When left unchecked, these humidity variations have consequences for people's health, electrical appliances, and agricultural products with a corresponding detrimental effect on the environment.

Therefore, to have a desirable atmosphere, it is essential to monitor, detect and control the ambient humidity under different conditions ranging from low to high temperature or in mixtures with other gases by precise and provident sensors.

In the light of this, Dare and Adanu-Ogbole (2022) developed highly sensitive humidity sensor based on porous Ag-ZnO core (56 nm)-shell (11 nm) nanorod and nanocomposite. The preparation of Ag–ZnO nanocomposite was followed by characterization using EDX, XRD, SEM, and TEM. Film of the Ag– ZnO was prepared by coating the Ag–ZnO on glass substrate and digital electrode. The sensor element (Ag–ZnO) was placed inside a fabricated humidity glass chamber illustrated in Figure 17

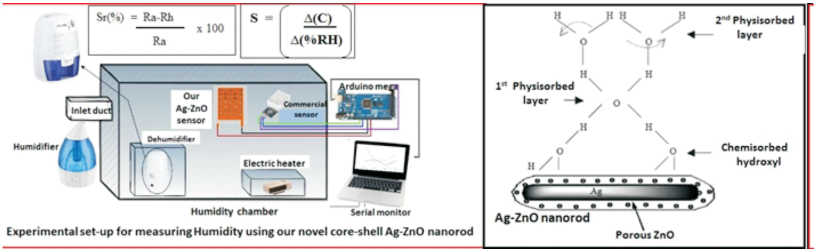

Figure 17: Fabricated glass chamber for humidity sensor and mechanism

The humidity testing of the sensors was conducted using a proton-type dynamic humidity chamber and the humidity was maintained in the range of 10%RH to 100%RH at room temperature. The electrical conduction in a proton type humidity sensor is basically explained by the water adsorption mechanism. Water is adsorbed onto the metal oxide surface and also onto the capillary water condensation within the pores. At the initial stage of adsorption, the negatively charged oxygen is electro statically attached to positively charged metallic ion of the sensor material to form hydroxides. Thus, the grain surfaces which are contiguous to the pores are covered by a chemisorbed monolayer. As humidity increases, the first physisorbed layer localized by hydrogen bonding of a single water molecule disintegrates to two surface hydroxyls. A hydroxonium group, H_3O^+, is thereafter formed through that molecules in the second layer which are on the average singly hydrogen bonded to the underlying layer. The proton moves freely along the water layer and thus determines the sensor conductivity, resistivity and overall sensitivity, which were calculated accordingly.

The study finds that sensitivity increases with relative humidity at a 10%RH interval. Ag-ZnO sensor exhibits a higher sensitivity of 687Hz/%RH in comparison to ZnO nanosensor which has a maximum sensitivity of 324 Hz/%RH. The increase in sensitvity of Ag-ZnO can be attributed to the high surface area of absorption present in porous ZnO shell and the electrical capability of Ag core in transducing the water vapour absorbed into electrical signals. The Ag-ZnO and ZnO sensor exhibits a fast response and recovery time of 54s and 73s, low hysteresis of 3.76%RH and 5.2%RH respectively. The result of the variation in resistance against relative humidity (RH) reveals a greater significant factor (SF) of 5.25 for Ag-ZnO and 1,88 for ZnO. The hybrid of Ag-ZnO nanocomposites proves to be a better humidity sensor and can serve as replacement for many other materials for humidity sensor currently in circulation in the market. Its further preliminary real-time humidity measuring in wireless communication using Internet of Things (IoT) requiring WiFi,microcontroller, antenna made it possible to extend applications to smart homes and agricultural practices from data received via smartphones.

3.7.3 *Antimicrobial activities, controlled release profile for wound dressing and hyperthermia release of active potential drugs*

As infections caused by antibiotic-resistant microorganisms are a matter of global concern, AgNPs arise as an excellent alternative as they can be applied to prevent infections caused by these microorganisms, decontaminate medical supplies, and even combat infections in course. As an antibiotic alternative, this application has been broadly studied in recent years with the objective of developing new antimicrobial products for decontamination or infection treatments taking advantage of the already established knowledge about their efficiency even against multidrug resistant organisms.

Foodborne and waterborne illnesses have emerged as a major public health concern around the world. WHO (2014) reported that there is about 30% of the population in industrialized countries affected by foodborne diseases every year. The consumption of foods contaminated with foodborne pathogens such as bacteria, fungi, viruses, and toxins are often recognized as the main source of foodborne illness in humans.

Dare *et al*. (2012), Dare and Akinsiku (2019,2020,2020) have investigated the antimicrobial properties of green synthesized AgNPs and allied by evaluation of sensitivity and testing Minimum Inhibitory Concentration (MIC), Minimum Bactericidal Concentration (MBC) and Minimum Fungicidal Concentration (MFC) tests showed the activities of Ag and Ag/Ni nanoparticles on S. *aureus, S. pyogenes, E. coli, P. aeruginosa, C. albicans* and *T. rubrum*.

The results when compared with the control Ciprofloxacin (Bacteria) and Fluconazole (Fungi) are strongly indicative of potential attributes of AgNPs and Ag-Ni . Antimicrobial activity as determined by measuring the zone of inhibition around each well (excluding the diameter of the well) for each nanoparticle obtained from the plant extract compares favorably with ciprofloxacin and fluconazole. Incorporation of AgNPs into biodegradable biopolymers has been a hot research in the development of antimicrobial plasters used in medical wound dressings.

However, in recent years, biodegradable chitosan have attracted attention of researchers as carriers for drug delivery system, host materials for AgNPs nanoparticles, as well as other stabilizing agents. However, appropriate release profile of antimicrobial AgNPs from its host remains a challenge. Dare and Sonde (2016); Dare and Olaniyan (2016); Dare and Ogungbesan (2016) have carried out preparation of AgNP-Chitosan film, studied swelling property, in vitro (phosphate buffer (pH 7.4) at 25 °C.) release study of silver from chitosan-silver nanocomposite and antimicrobial activities of the synthesized films were tested against human pathogens like Staphylococcus aureus, Shigella dysenteriae, Escherichia coli, Salmonella typhii and Klebsiella pnueumoniae to establish the nanocomposite potentials in wound dressing. Crosslinked chitosan-silver nanocomposite demonstrated a slower release pattern relative to un-crosslinked chitosan-silver nanocomposite. The crosslinked and un-crosslinked nanocomposite became dislodged and completely released at 120 minutes and 90 minutes respectively. The results of the antibacterial activities revealed that the cross-linked chitosan-silver nanocomposite film has higher antibacterial properties than un-crosslinked chitosan-silver nanocomposite films. This study provides chitosan nanocomposite films potentially useful for delivery system.

3.7.4 *Dye sensitized solar cell (DSSC) based on ZnO-dye nanocomposite*

The use of dye sensitization in photovoltaics has received a great interest after the breakthrough achieved by in the early 1990s. They developed a DSSC with energy conversion efficiency exceeding 7% in 1991 and 11.4% in 2001 by combining nanostructured electrodes to efficient charge injection dyes. Since then, TiO_2 nano-particle films have been widely investigated for DSSCs. However, TiO_2 films have some defects such as lack of enough energy barriers between the interface of the films and electrolytes. Laali, as popularly called, is grown in the savannah region of West Africa and are used as colouring material in the designing of fashionable tattoos on human bodies. Lawsonia inermis (Laali) is a very popular natural dye used in colouring fingers, hands, nails and hair (in northern part of Nigeria). The pyhtochemical mainly found in *Laali* stem bark is called Isoplumbagin. *Zobo* (Hibiscus sabdarifa) richly contains anthocyanin pigment, and is responsible for its red or wine colour. Dare and Bada (2017) prepared ZnO–laali, ZnO–zobo or ZnO–methyl red for the purpose of an enhanced optical properties and photosensitization suitable for DSSC.

Dare and Bada (2017) have considered *Laali* and *Zobo* (natural dyes) and methyl red (synthetic dye) for the sensitization of ZnO nanoparticle while investigating the optical properties of the hybrid nanocomposites. The natural dyes have been considered because of their good standing photochemical and phototherapeutic applications. Wet chemistry hybridization protocols have been followed which successfully led to inorganic–organic dye nanocomposites (ZnO–laali, ZnO–zobo) as determined by XRD and SEM.

There are evidences that isoplumbagin and anthocyanin that are, respectively, present in Laali and Zobo, successfully anchored themselves on ZnO surfaces. In this regard, methyl red behaves differently as a result of its acidic nature which undermined its stability and prevents anchorage. ZnO–laali and ZnO– zobo have demonstrated enhanced absorption and optical properties with evidence of electron injection from the dyes into ZnO scaffold. Contrary phenomenon was displayed by ZnO–methyl red. Overall, by nanoengineering these two materials into a single motif, the ensuing hybrid nanocomposite would not only exhibit the unique properties of dyes and the semiconductor, but also generate novel collective phenomenon based on the interaction of isoplumbagin or anthocyanin with ZnO. Indeed, ZnO–laali, in particular holds a significant promise for application in dye-sensitised solar cells.

3.8 My contributions in sustainable nanotechnology

My recent innovatively invoked research revolved around sustainable nanotechnology, which allows cautionably sensible and maximum utilization of biodiversified bioresources and discarded wastes respectively as nanostructuring ingredient for the benefit of mankind. Natural resources and raw materials are the physical foundation of the world, which are the initial requirements for the growing economy. However, most of these

valuable resources eventually end up as waste materials.
Sustainable nanotechnology is the development of science and technology within the1-100 nanometer scale, with considerations to the long-term economic viability and a sensible use of natural resources, while minimizing negative effects to human health and the environment. Sustainable nanotechnology remains a green nanomaterial for clean environment and tendency towards waste reduction via reuse, repair and recyle.

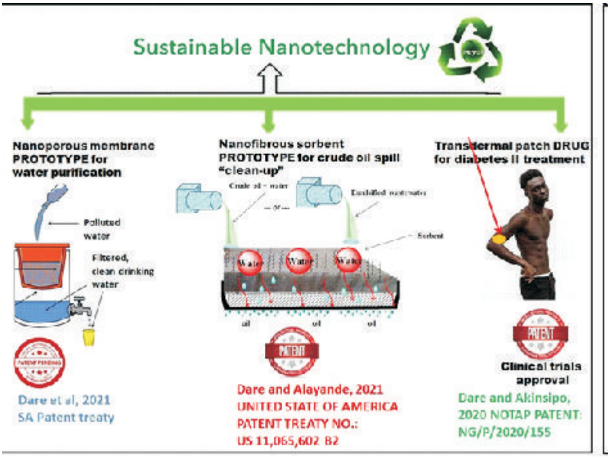

Figure 18: My specific innovative and inventive contributions in membrane technology, crude oil spill —cleanup prototype and transdermal drug delivery

My research outfit in this direction covers (Figure 18): (1) Nanoporous membrane technology for water purification (Pending patents, Dare and Soboyejo, 2011; Olubayode *et al* 2017, (2) Nanofibrous sorbent for crude oil spill "clean up" and oil/water separation (Dare and Alayande, 2021, UNITED STATE OF AMERICA PATENT TREATY NO.: US 11,065,602 B2; Dare and Alayande (2018, 2016, 2016) (3) Nanomedicine with special focus on novel drug design and delivery (Dare and Akinsipo, 2020: NOTAP PATENT: NG/P/2020/155; Dare and Akinsipo 2020 ; Bamisaiye *et al*. 2017).

Figure 19: Discarded wastes and biomass used for my sustainable nanotechnology project

As we all know that as much as Nigeria is endowed with biodiversity bioresources, however unfortunately, we are top world linear economy giant with overwhelmingly un-recycled discarded wastes constituting environmental nuisance. For us to step into circular economy, sensible utilization of biodiversity and maximum recycling/re-use of discarded wastes in nanostructuring becomes a necessity. In this view, I have engaged Nigeria based bioresources, discarded wastes and non-toxic friendly chemical (Figure 19) in nanotechnology for unprecedented applications in fulfillment of circularity.

3.8.1 *Development of Point-of-Use (POU) nanoporous membrane prototype for water purifications*

I was privileged to be one of the major resource persons alongside Nigerians in diaspora (Prof. Wole Soboyejo and Prof. Niyi Babatope) in the Nigeria Nanotechnology Initiative (2006), which brought nanotechnology into limelight in Nigeria. The NNI was sponsored by Ministry of Science and Technology and NASENI. The NNI inauguration and readiness of FG under President O. Obasanjo to accept nanotechnology as the next industrial revolution prompted my research in this field having recognized access to potable water as a major challenge in Nigeria. Having visited Princeton University, NJ, USA and which prompted a return visitation of my American collaborators to Nigeria in 2010, we kick-started **developmental stage 1** research on sustainable membrane technology for water purification while utilizing clay, plastic clay, kaolin, saw-dust and colloidal AgNPs as ingredients for water filter formulation which follows underlined processing involving proportional mixing of plastic clay and saw dust before casting into frustum shape. Subsequent firing in a kiln at 900°C expelled combustible saw dust and resulted to porous water filter. For antimicrobial activity, the filter must be coated with colloidal AgNPs solution. We characterized the water filter while evaluating mechanical properties and filtration efficiency before testing its effectiveness to remove pathogens. The formulated water filter demonstrated effectiveness in removal of bacterial and dissolved chemicals with 95.2% efficiency (Figure 20A)

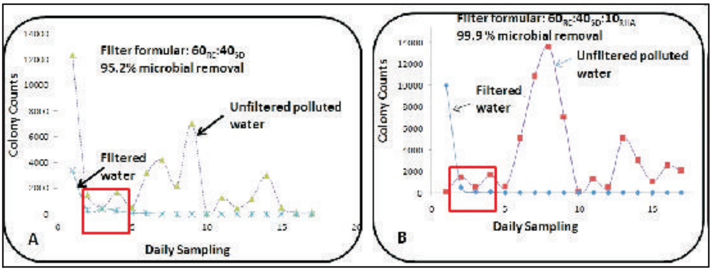

Figure 20: A, Microbial filtration using developed water filter prototype made from red clay, saw dust and colloidal AgNPs. B, Microbial filtration using developed water filter prototype made from kaolinic clay, saw dust, nanoporous silica and colloidal AgNPs

lter prototype made from kaolinic clay, saw dust, nanoporous silica and colloidal AgNPs

With these results at hand, we felt the need to proceed to a field study on the Use of Clay Ceramic Water Filters and Influences on the General Health in Nigeria (Dare and Soboyejo, 2011)

Field study and surveys were conducted to evaluate interdisciplinary parameters influencing the health of people using ceramic filters for water purification. A total of 52 families were distributed with filters at Eweje Village, Odeda Local Government Area, Ogun State, Nigeria. Surveys contained questions related to hygiene, health, water source and treatment, socio-economic and educational status of people and their use of clay ceramic water filters. Several parameters were studied including time of use of water filter, maintainability, education, societal economics, and the social status of the people using the filters. There was interdependence between these parameters. Health of the Eweje village community was greatly influenced by the number of people using the filter, the time of filter usage, education, maintainability, access to medical facilities, and economic status. A novel multi parameter multivariate regression approach clearly enumerates the hierarchy of the effects of the influencing variables on the health of Eweje community. Apart from population and time of filter use, access to medical services also influenced health of this rural community. After a prolong usage, we detected ineffectiveness of the water filter arising from enlarged and torturous porosity outside nano-range allowing entrance of pathogen. We also observed feeble nature of water filter undermining mechanical strength. This incidental phenomenon led us to further **Developmental stage 2**, which was carried out in my laboratory after the departure of my collaborator to the USA.

Developmental stage 2: This stage which necessitate an improvement upon stage 1 entails substituting red clay with plastic kaolinic clay, adding as-prepared additional nanoporous silica to nanocast torturous porosity with the view for regularly ordered porosity and eventually come out with optimized formular (60RC:40SD:10RHA).

The results obtained represent an improved version with the filter possessing enhanced mechanical property, moderate filtration efficiency (2.5 L per hours) and demonstrate adequate propensity to remove 99.99% pathogen (Figure 20B). More importantly, there was transition from disordered to ordered porosity averagely 62.8 nm.

Figure 21: Demonstration of my water purification technology before NUC assessors, Minister of State (now Governor Y. Wike of River state), the press and eventual NURESDEF award as 2nd best in Nigeria

Mr Vice Chancellor, I am pleased to inform you that second stage water filter prototype efficiency integrity (Fig. 21): (1) was demonstrated before government functionaries (2) was demonstrated in the air (NTA and AIT) under "Voyage of Discovery" sponsored by NUC (3) was accorded an award of excellence and 2nd position overall (NURESDEF 2012) held at NUC, Abuja.

3.8.2 *Developmental stage 3: My inventive research contributions in the development of porous sorbent and its hybrid for crude oil spillage "clean-up", oil/water separation and eventual water purification*

With the increase of offshore drilling of oil, production and transportation, the chances of oil spillage has enormously increased. Oil spillages have a catastrophic impact on our aquatic environment and ecosystem. The Niger Delta region of Nigeria in particular is witnessing serious environmental discomfort arising from various level of oil spillage and this has undermined socio-economic status of their communities. Ground and surface water, which could have been useful are contaminated making drinkable water a problem. In the last few years, development of special wettable materials for oil-water separation has received tremendous research and industrial interest. Materials with selective wettability, that is superhydrophobic and superoleophilic, or superhydrophilic and superoleophobic, can be used to remove only one phase from the oil/water mixture. Moreover, the effect of the surface chemistry and surface architecture can further promote the superwetting behaviour and improve separation efficiency. In the year 2012, I strongly felt the need to contribute into research revolving around environmental remediation with a particular focus on how to partly solve crude oil spillage "clean-up" problem in Niger Delta and create platform for purification of not only crude oil-contaminated water but also emulsified wastewater. In view of this, I assigned Samson Alayande, now an Associate Professor, Minnesota University, USA, to carry out his Ph.D project in this field. With the view to ameliorating the aforementioned challenges facing this region, while focusing on crude oil spill clean-up, point-of-use clean and potable water, efforts were made to re-use expanded polystyrene (EP), a discarded electronic and take-away food packaging wastes that constitute disposal problem, for the development of superhydrophobic and superoleophilic surface for de-watering/de-oiling of crude oil. Using electrospining nanostructuring techniques, superhydrophobic and superoleophilic surface of porous beaded electrospun EP and EP – zeolite fiber for crude oil/water and emulsified wastewater separation were developed (Dare and Alayande, 2016). The hybrid film (EP, EP/Zeolite), fibers (beaded EP and EP/Zeolite) exhibited superhydrophobic and superoleophilic wetting properties (water contact angle > 150^{o}; oil contact angle = 0^{o}) which has a full capability to separate oil/water mixture and eventual crude oil spillage —clean-up (Figure 22).

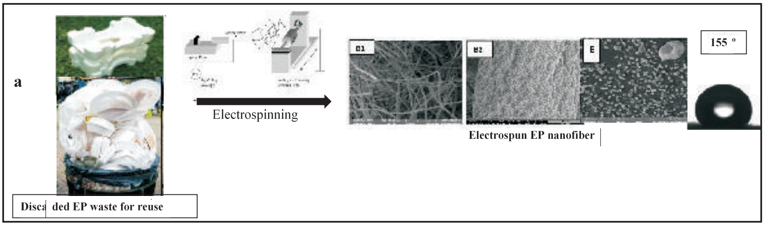

Figure 22: Nanofibrous sorbent development from discarded EP wastes, SEM and water contact angle results

Mr. Vice Chancellor, distinguished Professors and colleagues, I am delighted to inform you that the project from which a FUNAAB-awarded Ph.D thesis of Dr. Samson Alayande evolved yielded an invention. This INVENTION (Dare and Alayande, 2021: UNITED STATE OF AMERICA PATENT TREATY NO.: US 11,065,602 B2) relates to the recovery of crude oil from a crude oil adsorbent and simultaneously regenerating the crude oil adsorbent. The invention also provides a method of treating crude oil-contaminated water to remove crude oil therefrom. Furthermore, the invention provides a process installation and plant set-up for future industrial processing of crude oil contaminated water common in OPEC countries, especially Niger Delta region of Nigeria.

Subsequently, the invention provided a reason to look into household unit adoption of this prototype POU basis to be able to decontaminate the oil-contaminated water making the water suitable for drinking purposes. To do this requires the marriage of our invention with stage 2 developmental prototype. This entails making our ceramic in stage 2 a support for various superhydrophobic or superhydrophilic surfaces involving hydrophobic silica aerogel or hydrophilic silica aerogel respectively. The de-oiled water permeate could further encounter nanoporous carbon block which finally remove other microbial and chemical contaminant making the water eventually suitable for drinking and can be used at POU.

3.9 My inventive research contribution in nanomedicine: drug design and delivery for type 2 diabetes mellintus treatment

Diabetes Mellitus (DM) is a metabolic disorder characterized by a persistent rise in blood glucose level (BGL) caused by ineffective insulin function, secretion, or both. DM type II, a non-insulin dependent, is the most common form of the disease, accounting for 90-95% of cases in which the body does not produce enough insulin or properly use it depending on the state of β-cell.

So far, the accessible medicines for DM are various preparations of insulin and oral antihyperglycemic agents. The older conventional oral hypoglycemics are sulphonylurea, alpha-glucosidase inhibitors, biguanides e.t.c while the newer medicines include glucokinase activators and injectable glucagon-like peptide. Unfortunately, both conventional and newer agents are still with their shortcomings and therefore successful treatment of DM remains a global challenge requiring further investigation. Undoubtedly, these medications are associated with unnecessary drug reactions or side effects, including hepatocellular injury, exacerbate renal diseases, blood dyscrasias, gastrointestinal irregularity, hypoglycemias, hypersensitivity reactions e.t.c

As much as both medication types are defective and problematic after long usage, it is also unfortunate that their oral mode of administration leave much to be desired as it promotes further severe health complications arising from **1st pass metabolism**.

Transdermal system by delivery drugs across the skin into systemic circulation resist the alteration in absorption rate, metabolism and prevent gastrointestinal adverse effect occurring during oral administration of drugs. It is idealy suited for chronic disorder. It allows the administration of potent drugs with the benefit of self-administration and enhances therapeutic efficacy. However, transdermal system functions in the presence of a carrier, which could be nanoemulsion. Nanoemulsion has been anticipated as the best drug delivery nanocarrier for transdermal application because of its uniqueness in exclusive interaction with the skin cells, its prominent fluidic nature, high permeability and efficient protective ability for incorporating drugs. Several reports have confirmed these promising nanoemulsified techniques toward enhancement of transdermal drug permeation as it greatly a barrierconquerring system that helps overcome associated skin challenges. The system uniquely trespass the skin barrier and deposit drug on site.

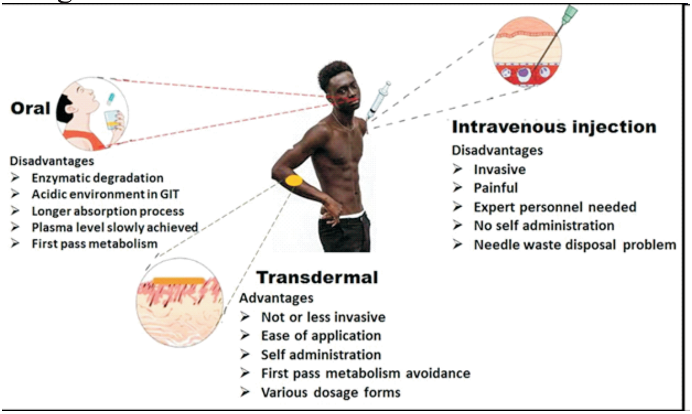

Figure 23: Comparison of various drug delivery methods: Oral, IV and Transdermal

Having understood the overriding advantages of transdermal drug delivery over both oral and intravenous injection (Figure 23), we felt the need to explore both chemical and medicinal plant phytoactive molecule as anti-hyperglyceamic anti-diabetes drugs for transdermal application in-vivo. This was a Ph.D. project which I assigned to Basirat Akinsipo and Yomi Bamisaiye and Titilayo Adebowale who carried out novel phytodrug and conventional chemical respectively for diabetes treatment in-vivo and in-vitro.

Two-third of the world identified medicinal plants (MP) containing phytoactive isolated drugs for hypoglycemic activitiy are in Nigeria (Google scholar and scopus search). One-third of the phytochemicals in MP in Nigeria have proven records (in-vivo and clinical) for treatment of T1DM and T2DM orally. Unfortunately, there is no record in Nigeria against transdermal route of phytodrug for hypoglycemic activity.

In search of alternative to oral drug delivery, we have incorporated ciprofloxacin synthetic drug in nanoemulsified system for transdermal delivery in-vitro (Bamisaiye et al. 2017).
In another quest for alternative to conventional synthetic drug, Dare and Oyelaja-Akinsipo (2020) , as basis for comparison utilized nanoemulsified diosgenin phytodrug for transdermal route treatment of T2DM in both rat and zebrafish model where protective roles of diosgenin against hyperglycaemiamediated cerebral ischemic brain injury were unfolded.

Zebrafish (Danio rerio) is undergoing wide exploration as an animal model in disease discovery, disease development and drug discovery due to their fertility and unique genetic and physiological similarity as that of mammals. The study aimed at studying the glucose-regulating effect of Diosgenin in an STZinduced type 2 diabetes Zebrafish model including the possibility of hyperglycemic-mediated cerebral ischemic damage while presenting a mild exploration of DG towards its neuroprotective role against resulting traces of brain injury.

Diosgenin selectively lowers the blood glucose concentration in a hyperglycemia-induced diabetes condition. It improves the weight and growth pattern of diabetic zebrafishes and also displayed enhanced catalytic activity. Its activity towards protecting the brain from the possibility of hyperglycemic-mediated brain damage and apoptotic brain cell death is visible from the suppressed inflammation. This study set forth the possibility and potential of diosgenin as an anti-inflammatory and antidiabetic and neuroprotective agent. Its neuroprotectant potential can be positively explored in future clinical studies.

The properties that have been considered as overriding effective therapeutic potentials of phytodrugs for T2DM managements are (1) MP phytochemicals having not only antihyperglycemic but also insulinomimetic activities (2) Phytodrug possessing ability to target multiple therapeutically-relevant proteins of diabetes unlike synthetic metformin and other like drugs.

Hence, we have selected carefully MP grown on Nigeria soil primary phytochemicals (Quercetin, Vitexin, Alstonine, Allicin, Mangiferin, Moringinine and Chlorogenin) based on their potential to be (1) nanostructurally incorporated in globular droplet nanoemulsion in size < 100 nm (2) interact and modulate multiple diabetes relevant proteins (3) possess insulinomimetic properties (4) proven orally administered in-vivo and clinical trials which provided a basis for the our transdermal delivery of nanoemulsified phytodrug for T2DM management.

A novel formulation that uses natural extracts to produce an oil-in-water nanoemulsion matrix that engulfs and protects the drug diosgenin to ensure bioavailability, safety, targeted and sustained delivery of the drug to its target has been developed. The nanoemulsion acts as a solubilizing, non-invasive protective drug carrier and permeating agent that is administered transdermally to treat Type II Diabetes Mellitus. Diabetic rats were prepared for transdermal treatment with the formulated diosgenin-innanoemulsion. 1.11 g of 20 mg/kg body weight (*bw*) diosgenin was applied at every single application 12 hourly for three weeks. The therapeutic potential of diosgenin against T2DM was determined by measuring the blood glucose concentration (mg/dL) and HbA1c (%) of treated rats at specific intervals.

The overriding result is a much more effectiveness in antihyperglycemic action via inhibition of αglucosidace, α-amylase, and DPP-4 enzyme e.t.c which serves to eventually promote insulin sensitivity, secretion and pancreatic β-cell nourishment.

As result example, it was evident that the blood glucose concentration in diabetic rats (DS-1 and DS-2) was highly elevated in comparison to the normal control (NC). With a single week's treatment of the rats using the formulation, the blood glucose concentration decreased significantly, with better results seen at early invention compared to late intervention. The blood glucose concentration for both early and late intervention cases decreased in week 2. In the early intervention cases, there was not a significant decrease in blood glucose concentration in week 3 of treatment, but there was a noticeable difference in the late intervention cases in week 3.

HbA1c (hemoglobin A1c) levels were highly elevated in diabetic rats (DS-1 and DS-2) compared to the normal control. With treatment of the rats using the formulation, HbA1c levels decreased significantly, with better results seen at an early invention compared to late intervention. The HbA1c levels in the early intervention cases decreased to below that of the normal control, and in the late intervention cases, the HbA1c levels decreased to the same level as the normal control.

We confirmed transdermal route arrangement for phytodrug delivery via rat skin into systemic circulation to be safe, and effective in managing T2DM. As we maximised and optimised nanoemulsion formulations using the concept of nanotechnology to develop nanostructured globules hosting the drug, we could observe that that the combined influence of oleic acid/surfactants ratio facilitated drug permeation process while breaking SC skin barrier for regulated and predetermined delivery of unique plant-derived antidiabetes drug into systemic circulation. Ultimately, comparative transdermally and orally administered phytodrug results would provide basis for immediate nearest future clinical trials having screened optimally the efficacy of seven Nigeria MP isolated phytochemicals for Type 2 diabetes management.

Mr. Vice-chancellor, sir, this is another inventive output for us which warranted NOTAP patents (Dare and Oyelaja-Akinsipo, 2020 NOTAP PATENT:NG/P/2020/155 entitled "A NANO-EMULSIFIED PHYTO-DRUG FOR TRANSDERMAL TREATMENT OF DIABETES".

3.10. My contributions to the global communities

Mr. Vice Chancellor, "The small thing of today is a prerequisite to next big thing, which is very small". It is on this premise of the very small things that I stand and projected to the world as a scholar, contributing to the body of knowledge for the benefit of mankind. Up to this moment of inaugural lecture, I reiterate that I remain the first and only Professor of Nanotechnology in Nigeria. Sir, don't be surprised to see almost everybody nicknaming me "The nano man". Significantly, I have taken the concept of "the very small of a thing" to promote the images of, not only FUNAAB, but also Africa, in the following respects:

1. I was one of the major contributors to the two consecutive 2004 and 2005 NURESDEF 1st position awards given to UNAAB where I showcased special glasses and engine lubricants nanoproducts. The parading assessors, one of whom happened to be DG NASENI. Late Prof. O. Adewoye raised an eyebrow for catching a glimpse at nanoproducts, which he overheard of, but never saw any until that moment. Prof. Adewoye gave me his card, and the next call of reference was from the PS, Ministry of Science and Technology
2. Nanotechnology was brought into limelight in Nigeria in the year 2006 with the inauguration of NNI at Hilton hotel in Abuja. The Federal Ministry of Science and Technology invited me as the major resource to deliver NNI inauguration keynote and subsequently draw a nanotechnology roadmap for Nigeria.
3. Ministry of Science and Technology invited me to serve as TRAINER of selected scientists, Professors, Industrialists from all over Nigeria in a 3-day workshop on the practicality of Nanotechnology in 2009. Two of our Professors in FUNAAB got trained.
4. I won an award as the 2nd best in individual R & D NURESDEF 2012 where I exhibited Nanoporous water purification technology. Subsequently, National University Commission put me on AIT and NTA for the demonstration of the invention under "Voyage of Discovery".
5. NASRDA-LAUTECH 2022 was a memorable one where I gave a keynote address in a conference/workshop with highly ranked (up to a Major General) members of the Armed Forces, PS and Minister of Science Technology and Innovation, Hon. Adeleke Mamora in attendance.
6. Let me quickly mention a striking one which projected nanotechnology impact and contribution to the international body.

   In the year 2017, I exported the concept of NANOFORENSIC relating to criminality fingerprinting detection to Regensburg University, Germany. The result obtained was awesome which prompted my host in Germany, a highly ranked Henseberg Professor, in person of Prof. Dr. David Diaz to pay Chemistry Department, FUNAAB a visit during which he delivered lectures and demonstrated practicals to students. Furthermore, Prof. Diaz, paid homage to FUNAAB staff school where he humbly presented gifts to pupils. We ended it in a social gathering attracting my mentees for a dinner at Sweet Sensation in Abeokuta.

Let me use this opportunity to thank the University Management and the entire Chemistry Department for the honour to host Hesenberg German Professor.

4.0. CONCLUSIONS

Mr. Vice Chancellor, the technological impact of the "very small thing" vis-à-vis the size-powered harbinger is underscored by the mentioned various unique contributions in nanotechnology which have revolutionalized advanced materials, sensors, catalysis, nanoporous membranes, drug delivery, drug design, lubricants, forensic e.t.c ended in innovations and inventions useful to mankind.

As nanotechnology is truly a size-powered harbinger, I have used all its strategic styles to create novel nanoparticles as small as 1.5 nm demonstrating unprecedented properties with multifunctional applications. In particular, my contribution in the development of nanofibrous sorbents for crude oil "clean-up" and spillage remediation is awesome leading to the first-ever nanotechnology patent coming from Nigeria in USA Patent treaty.

Moreoever, I have developed effective anti-hyperglycemic anti-diabetes nanoemulsified phytodrug possessing multi-docking character with diabetes proteins and insulinometic property for

skin patched transdermal application for diabetes management in animal model. This has appeared as another patent for which I have received a “go ahead” approval to proceed on “Placebo-controlled clinical trial” for application on humans.
The recent success of COVID-19 mRNA nanovaccine from Moderna and Pfizer/BioNTech are just two examples of how nanotechnology-enabled products can dramatically impact our health lives today and strengthened public trust in the concept. Therefore, nanomaterials have become ubiquitous in daily life and are now commercialized as commondity products with over five thousand nanotechnology based companies.

The global landscape of nanotechnology R & D has created a picture that highlights the extent to which nanodimension of a thing has captured the minds of several national government as key to progress. United Nations has identified nanotechnology as the key platform technologies for growth and developments.
Russian Pressident V. Putin stressed that “Russia needs an innovative army using nanotechnology to keep up in a new high tech arms race”. In his address to the Federal Assembly, Putin singled out nanotechnology as the locomotive of Russia's scientific and technological development strategy.

Former United State President Barak Obama stated “The potential for a technological revolution has inspired grand claims about its promises for development and progress to mankind”

Finally, nanotechnology represents a tip of the pyramid that is uncovered from the sand of ignorance. As scholarly activities all over the world dig this sand to uncover the giant strides of the very small particles, we shall see how exciting to have it as size-powered harbinger of the next technological and industrial revolution.

5.0 RECOMMENDATIONS

As recommendation and to be part of this technological revolution, our country may adopt the following practical action plans/steps needful to establish a robust nanotechnology program. These include but not limited to:

(1) The first one goes to FUNAAB, as there is a dire need for Institute of Nanotechnology and Advanced Materials. As mentioned earlier, nanoproducts exhibited in the NURESDEF 2004 and 2005 raised the eyebrow of assessors and it constituted one of the reasons for the awards given to UNAAB on those two occasions.

During my sabbatical at FULAFIA, I exhibited another dimension of nanoporous materials and a 2 year-old University for that matter, was rated 2nd in NURESDEF 2012.

The implication of this is the general view of nanotechnology as strategic concept underpinning next industrial revolution. Therefore, FUNAAB should not be left out of this.

(2) For FUNAAB, as we have set the ball rolling by having work done on the soil of FUNAAB registered in a world class Patent Treaty, USA, I recommend that our university should establish Scholars' Office of Patent, Intellectual Property Protection and Partnership. This would facilitate business development of research output

(3) For our nation, Department of Nanotechnology should be created under the Ministry of Science, Technology and Innovation with budgetary allocations to coordinate and oversee the general activities of nanotechnology.

(4) For Nigeria to be part of the next technological revolution coming from nanotechnology, Centers of Excellence in Nanotechnology with state-of-the-art equipment relevant to R & D in nanotechnology should be established. In this regard, appropriate policy and plans to back up

nanotechnology is urgently needed in Nigeria. South Africa and Egypt already have policy and plans on nanotechnology

(5) Envying and imitating those who have succeeded is not synonymous to weakness. However, building on their success stories is tantamount to advancement. Nigeria should build on the success stories of USA, Japan, Germany e.t.c to take our country to the next technological revolution through nanotechnology.

6.0 ACKNOWLEDGEMENTS

The ultimate measure of a man is not at a time of convenience, abundance and merriments but the time of controversy and challenges. I give God thanks for sailing through life challenges and abundant grace given me in getting to this enviable level in life.

I appreciate all the past Vice-Chancellors of this University and thanks to Prof. O. B. Oyewole during whose tenure I became a Professor. I am also very grateful to our current Vice Chancellor, Professor Olusola Babatunde Kehinde , who made it possible for me to be here giving the 78th in the series of FUNAAB Inaugural lectures. I equally appreciate the Principal Officers of the University- Prof. C.N. Ikeobi (DVCA), Prof. Kola Adebayo (DVCD), Dr. H. Adekola (Registrar), Mr. C. Ezekpeazu (Bursar) and Prof. N. Onifade (University Librarian) who also made it possible for me to be here today for a lecture.

I thank the Dean, College of Physical Sciences, Prof. T. Akinwale, for giving me the privilege and further encouraging me to present this inaugural lecture. I also thank all the past Deans of the College. The entire college members, both academic and non-academic are acknowledged. I offer special appreciation to past Heads, my colleagues and technologists in the Department of

Chemistry. In this regard, let me thank the present Head of Department, Prof. Sherif Adewuyi who encouraged me for this lecture.

I thank the University Community (Member of ASUU, SSANU, NASU and NAAT) for their past and present contributions to my success stories.

My special appreciation goes to Prof. (Mrs.) H. A. Bodunde, the Chairperson, and members of FUNAAB Publications Committee, and the editorial team.

I wish to acknowledge my teachers from primary school, Aipate Baptist Primary School, Iwo and Methodist Primary School, Isale-Aro, Osogbo, to my secondary school, Ataoja High School, Osogbo. Let me specially thank Mr. K. Akinwumi, the pioneer Principal who used his strict disciplinary measures to curb me from my addicted regularly swimming habit at Gbodofan/Osun River after every school hour.

I am highly grateful to a worthy teacher/lecturer and mentor, Prof. Emeritus Gabriel Ademola Olatunji, who brought me into academics and equipped me with strategies for internationalization, which I continue to adopt till date. Among my mentors, I also appreciate Prof. I.C. Eromosele who took time to educate me on how to write and publish in rewarding journal. My international mentors are acknowledged. I am thanking Prof. Takeshi Shiono of Tokyo Institute of Technology, Japan for his role in the knowledge I acquired in polymer nanocomposite. Prof. Ling-Kang Liu of Academia Sinica, Taipei, Taiwan is appreciated for taking me through sol-gel nanostructuring of POSS nanocomposite.

The contribution of Prof. Rick Register of Princeton University, NJ, USA is acknowledged. Prof. Dr. David Diaz and Prof. Dr. Todd Marder of Regensburg University and Wurzburg University, Germany, respectively, are appreciated for allowing me to export forensic nanochemistry to their laboratories. As much as I had benefited from academic mentorship of the aforementioned, I did benefit from administrative mentorship of Prof. Mrs. Ekanem Braide, the pioneer Vice-Chancellor of Federal University Lafia (FULAFIA), for equipping me with rudiments of administration while I was pioneer Ag. Director of Academic Planning of FULAFIA. During my short one year sabbatical leave, as there was no DVC, she nominated me to represent her at: (1) the 27th Annual Conference of Association of Vice-Chancellors held at Nasarawa State University, Keffi in 2012 (2) Internationalization of Universities held at UN building, Dubai, UAE in 2012.

Prof. Mrs. C.O. Eromosele is on the list of my administrative mentors. Thanks is due to her for nominating and guiding me as Head of Department, Chemistry, FUNAAB between 2015 and 2017.

To my numerous former and present research students (both undergraduates and postgraduates), thank you for your dedication and hardwork including your contributions to some of the research results presented in this lecture. Special mention must be made of my past doctoral students whose theses I supervised on major term: Dr. Joseph Adekoya, an Associate Professor at Covenant University, Ota; Dr. Samson Alayande, an Associate Professor at Minesota University, USA; Dr. (Mrs) Bola Akinsiku, a Senior Lecturer at Covenant University, Ota; Dr. Wasiu Ayinde, a Research Fellow at Capetown University, South Africa; Dr. Idowu Sonde, Second-in-Command, TRACE, Ogun State; Dr. Kehinde Sodehinde, Senior Lecturer, Federal University, Oye-Ekiti; Dr. (Mrs) Basirat Oyesolape-Akinsipo, a Lecturer I at TASUED, Ijebu-Ode; Dr. Smart Olubayode, former Ag. MD, EMDI, Akure;

Mrs. Blessing Adanu; Mrs Yinka Olaniyan and Mrs. Shephra Ogungbesan.

By His grace, in the next one to two years, I shall be Professor of Professors as two of my former doctoral students ascend to their full Professorial cadre.

Many of my research accomplishments and internationalization have the financial supports of international research foundations and a few local trust funds.

MONBUSHO/UNESCO is appreciated for funding my research while I was a fellow at Tokyo Institute of Technology, Japan. Taiwanese NSF is acknowledged for providing me funds for my research activities at Academia Sinica, Taipei, Taiwan. Thanks is due to ICTP and TWAS for granting me equipment funds and facilitating my training activities in Trieste, Italy.

I am highly delighted to acknowledge USAMI/FULBRIGHT foundation for funding my research at Princeton University, NJ, USA. Thanks to NANOAFNET and Royal Society of Chemistry (RSC) for making me a member and also funding many of my research travels to South Africa, Ethiopia and Kenya. Above all, the incredible and invaluable research funding contributions provided by Alexander von Humboldt for my two-times research sojourn to Germany is appreciated.

FUNAAB RESDEC and TETFUND have supported my research twice through its IBR funds, Thanks. I cannot forget the benefactor roles played by Prof. Wole Soboyejo who shared his NSF with me to be able to conduct research on membrane technology.This is appreciated, Sir.

I wish to appreciate my late Parents, Bishop Amos Sobalaje Dare and Rachael Omobonike Mulikat Dare whose contributions to my general upbringing remain colossal and invaluable. Interestingly, they educated me up to the start of my Doctoral studies. My father's callings as a clergyman and my early lives in mission houses in Ijabe, Oka-Akoko and Ijebu-ode diocese molded me significantly.

At this juncture, let me appreciate my siblings: my brothers Mr. Kayode Dare, Mr. Segun Dare, Late Tunde Dare and Mr. Seun Dare and my sisters - Mrs. Funmilayo Bamgbade and Mrs. Yetunde Adediji.

There are special in-laws that portray themselves as family blood members in contributions. I stand to mention with gratitude to Mr. Funso Bamgbade, Mr Etiebet, Mrs Victoria Masika and Dr. Mrs. Sade Dare. I also appreciate greatly the contributions of late Alhaji Hon. Sulaiman Amusat and Mrs. Amudalat Adepoju.

My father's best friend is like another father whose contributions are noteworthy; it is no other than Late Rev. T. Iyiola Olasinde and Mrs Ibironke Olasinde. In this lineage, I appreciate my best friend, Mr. Abolade Gbenga Olasinde. I remember our childhood days as we copied each other in many respect to ascend in many life issues. Engineer Olawale Olasinde and Mr. Bode Olasinde are incredible giants in my life success stories. Thank you, brothers.

Mr. Saka Tinuola and Late J. Olasinde (Senior) hosted and guided me when my parents were on transfer to start God's ministry in Ijabe. I appreciate you greatly.

I cannot forget to appreciate Late Rev. Jeremiah Olaniyan and Mrs Olaniyan. They hosted and guided me while I lived with them at First Baptist Church, Okeesa, Iree and Calvary Baptist Church, Samaru, Zaria. In this lineage, I appreciate Mrs. Olanike Yeku, Mrs. Mojisola Olaniyan-Alabi, Mr. Taiye Olaniyan and Sister Bisi Kehinde.

My family: Mrs. Ima-Ima Dare, Engineer Mrs. Ayobami Dare, Master Israel Dare, Miss Priscilla Dare, Master Wilson Dare are appreciated for their endurance, especially most times I was not available around them. You have given me treasures which remain my life hopes.

Mr. Vice-Chancellor, Sir, Principal Officers of the University, distinguished colleagues, invited guests, ladies and gentlemen, greatest FUNAABITES, I thank you most sincerely for your patience and attention. God bless you.

Finally join me as I conclude this lecture with this hymn:

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ISBN: 978-978-799-092-6