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in Sri Lanka

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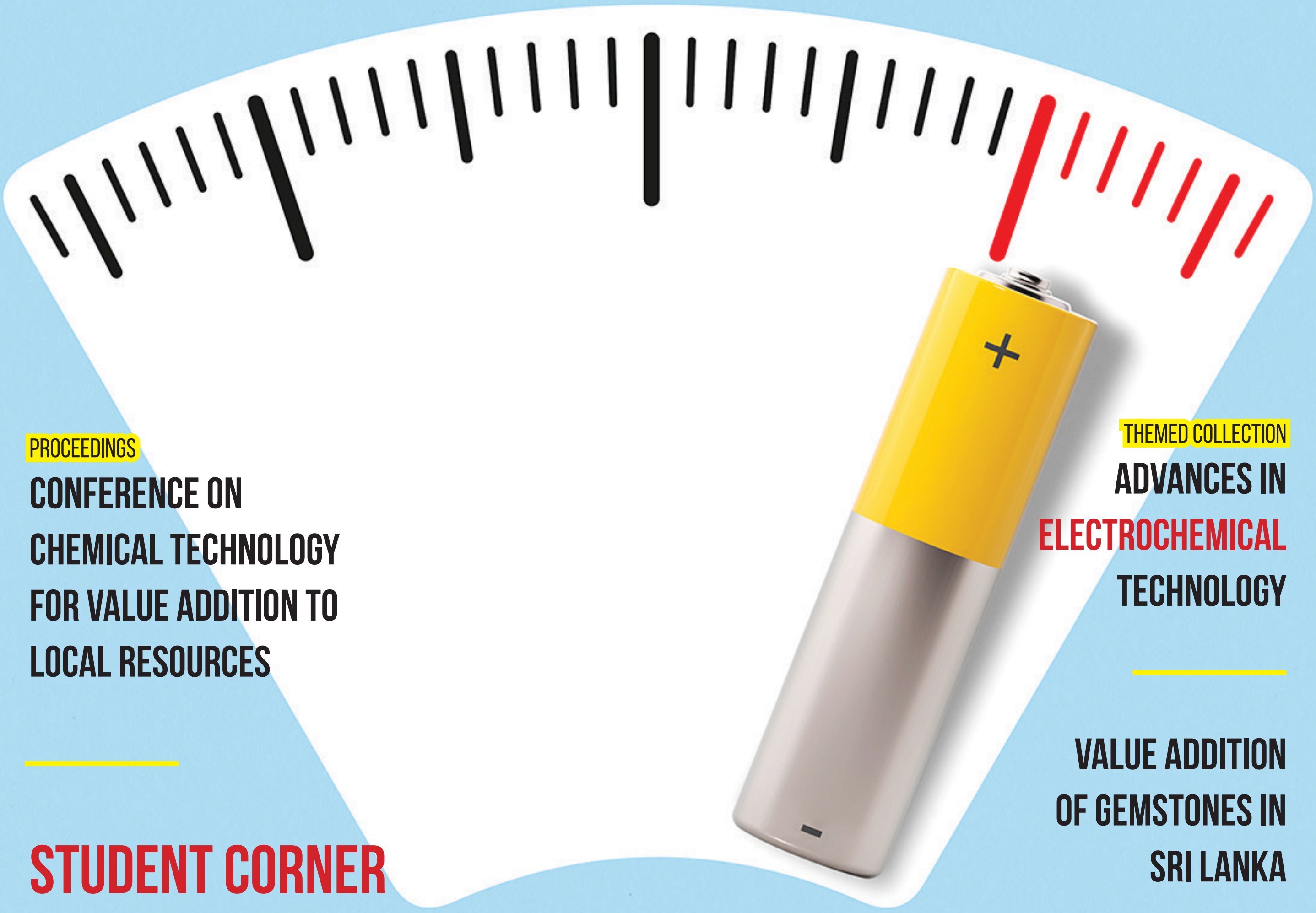

PROCEEDINGS

CONFERENCE ON CHEMICAL TECHNOLOGY FOR VALUE ADDITION TO LOCAL RESOURCES

STUDENT CORNER

THEMED COLLECTION

ADVANCES IN ELECTROCHEMICAL TECHNOLOGY

VALUE ADDITION OF GEMSTONES IN SRI LANKA

Chemistry in Sri Lanka

ISSN 1012 - 8999

The Tri-Annual Publication of the Institute of Chemistry Ceylon

Founded in 1971, Incorporated by Act of Parliament No. 15 of 1972

Successor to the Chemical Society of Ceylon, founded on 25th January 1941

Vol. 37 No. 1 **January 2020**

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Conference on Checmial Technology for value addition to local resources

Guest Editorial

Themed Collection : Advances in Electrochemical Technology

Natural Resources in Sri Lanka

Guest Articles

Student Corner

Theme for the year -

Shaping Careers of Chemists Through Advancement of Chemical Technology

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Outline of our Institute

The Institute of Chemistry Ceylon is a professional body and a learned society founded in 1971 and incorporated by act of Parliament No. 15 of 1972. It is the successor to the Chemical Society of Ceylon which was founded in 1941. Over 50 years of existence in Sri Lanka makes it the oldest scientific body in the country.

The Institute has been established for the general advancement of the science and practice of Chemistry and for the enhancement of the status of the profession of Chemistry in Sri Lanka. The Institute represents all branches of the profession and its membership is accepted by the government of Sri Lanka (by establishment circular 234 of 9-3-77) for purposes of recruitment and promotion of chemists.

Corporate Membership

Full membership is referred to as corporate membership and consists of two grades: **Fellow (F.I.Chem.C.)** and **Member (M.I.Chem.C.)**

Application for non-corporate membership is entertained for four grades: Associate (former Graduate) (A.I.Chem.C.), Licenciate (L.I.Chem.C.), Technician (Tech.I.Chem.C.) and Affiliate Member.

Revision of Membership Regulation

All Special Degree Chemists can now apply directly to obtain Associate (Graduate) Membership. Three year B. Sc. Graduates (with an acceptable standard of Chemistry) can

(i) directly become Licentiate

(ii) obtain corporate membership in a lesser number of years.

Tech.I.Chem.C.

Those who have passed the DLTC examination or LTCC examination or have obtained equivalent qualification and are engaged in the practice of Chemistry (or chemical sciences) acceptable to the Council are entitled to the designation Tech.I.Chem.C.

Members/Fellows with Membership for Life are entitled to the designation of **Chartered Chemist (C.Chem.)** on establishment of a high level of competence and professionalism in the practice of chemistry and showing their commitment to maintain their expertise.

All corporate members (Members / Fellows) are entitled to vote and become Council/ Committee members whether Chartered Chemists or not.

Membership Applications

Any application for admission to the appropriate class of membership or for transfer should be made on the prescribed form available from the Institute Office.

Current Subscription Rates

Fees should be payed on 1st of July every year and will be in respect of the year commencing from 1st July to 30th June

Fellow	Rs. 2000
Member	Rs. 2000
Associate	Rs. 1500
Licenciate	Rs. 1200
Technician	Rs. 750
Affiliate	Rs. 1200
Membership for Life	Rs. 15000

Entrance Fee

All the grades	Rs. 1000
Processing Fees*	Rs. 500
Processing Fee for Chartered Chemist designation	Rs. 5000
Institutional Members	Rs. 2500

*per application for admission/transfer to any grade

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CHEMISTRY IN SRI LANKA

Chemistry in Sri Lanka is a tri-annual publication of the Institute of Chemistry Ceylon and is published in January, May and September of each year. It is circulated among the members of the Institute of Chemistry and students of the Graduateship/DLTC course and libraries. The publication has a wide circulation and more than 750 copies are published. Award winning lectures, abstracts of communications to be presented at the annual sessions, review papers, activities of the institute, membership news are some of the items included in the magazine.

The editor invites from the membership the following items for publication in the next issue of the Chemistry in Sri Lanka which is due to be released in May 2020.

- *Personal news of the members*
- *Brief articles of topical interests*
- *Forthcoming conferences, seminars and workshops*
- *Latest text books and monographs of interest to chemists*

All publications will be subjected to approval of the 'Editorial and Publicity Committee' and the Council of the Institute of Chemistry Ceylon.

Further, prospective career opportunities for chemists, could be advertised in Chemistry in Sri Lanka at a nominal payment. The editor welcomes suggestions from the members for improvement of the publication.

Conference on Checmial Technology for value addition to local resources

Conference Proceedings

Mineral Resources of Sri Lanka: Present use and Future prospects

O A Ileperuma

Emeritus Professor of Chemistry, University of Peradeniya

Sri Lanka is well known for its mineral resources and their utilisation from ancient times. There is archaeological evidence that we had iron working sites spanning 2000 years long and swords manufactured in Sri Lanka were exported to the middle east. There is also evidence of using copper during the time of Sinhala kings perhaps using the already known pyrite deposits at Seruvila. Arab traders came to Sri Lanka searching for valuable gems and gave Sri Lanka the name Serendib. Thorianite exported during British times were used by Marie Curie for her pioneering work in radioactivity. Some elements such as polonium and radon were discovered using our thorianite. Sri Lankan graphite with exceptional purity was exported during the pre-independence period.

Exploitation of mineral resources and value addition are not possible without a concomitant development of a chemical industry. Sri Lanka has an abundance of beach sands rich in titanium which are now exported in raw form and these can be utilized to extract titanium dioxide and titanium metal. Other beach sands rich in rare earths are found at Beruwela and these have a ready market in the electronics industry. Unfortunately, exploitation of this valuable resource stopped after the advent of the free economy. Graphite is still exported without any value addition and this can be used to manufacture crucibles, electrodes for batteries and also for more recent products high technology products such as carbon nanotubes. Radioactive minerals such as thorianite occur inland as well as in beach sands and this is an attractive export since it is the raw material for making nuclear fuel.

One of our best economic mineral resources is apatite rock phosphate at Eppawela. The reserve extends over 7 km^2 and about 125 m deep from the surface. It is estimated that the reserve consists of 60 million tons of apatite. It can be converted to single super phosphate by the addition of sulphuric acid which can replace all our current phosphate fertiliser imports. This will also save the government about Rs. 5 billion a year which we now incur as fertiliser subsidy.

Another mineral which can be upgraded is calcite which occurs at Balangoda. Manufacturing precipitated calcium carbonate can save millions in importing this for the toothpaste and paint industries.

Inn some cases, we have gone backwards such as the abandoning of a crucible factory using our own graphite. Also, the Paranthan chemical factory was abandoned due to terrorism and no action has been taken to restart this factory. Sulphuric acid is another chemical which is required for value addition to beach sands and this can be prepared easily from the sulphur removed from the petroleum refinery. Our economic planners should become aware of the potential of future mineral based industries augmented by the development of a chemical industry.

Professor O A Ileperuma *earned his Ph.D. in Chemistry from the University of Arizona, USA in 1976. He is currently an emeritus Professor, after having served for 44 years at the Department of Chemistry, University of Peradeniya. He has published over 70 research publications in International journals, has presented 44 communications and has been the editor of over 7 International conferences. Moreover, Professor Ileperuma has published around ten textbooks for the GCE (A.L.) syllabus. His research areas include studies on solid-state solar cells fabricated from dye-sensitized semiconductor nanostructures, air pollution, and acid rain monitoring, transboundary pollution and chronic kidney disease of unknown origin.*

Sri Lanka's Black Sand: Mirage or Rainbow?

Nilwala Kottegoda

Department of Chemistry, University of Sri Jayewardenepura

Titanium is the ninth most available and abundant element in the earth's crust where approximately 0.6% is comprised it. Titanium ores are commonly found in nature mainly as rutile (95% TiO_2) and ilmenite (53% TiO_2) which are important economic minerals. The value added products of Ti ores are pigment grade TiO_2, ferro-titanium and Ti metal. TiO_2 is a prime commodity, used primarily in the pigment industry while Ti metal is commonly used in many industries such as aerospace, medical and automobile due to its light mass, high strength, corrosion resistance, biocompatibility and high thermal resistivity. The landscape of the TiO_2 market is quite competitive and is heading towards consolidation and upstream vertical integration with top players such as DuPont, Tronox and CRISTAL acquiring other firms, seeking to secure feedstock supplies (TZ Minerals International, 2017). The mineral sands industry has been dominated by two major multinationals and that will continue for the medium-term.

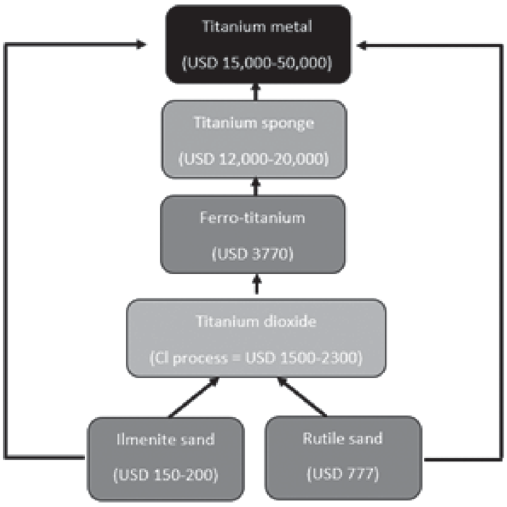

Figure1: Price of value-added products along the value chain for mineral sands. (All prices per MT are sourced from Alibaba.com and are subject to fluctuation)

Sri Lanka has large deposits of mineral sands scattered around the east coastline of the country and in Puttlam. The North-Eastern coastal line of Sri Lanka consists of approximately of 8 - 9 million tons of ilmenite, 1 million tons of rutile with a heavy metal content of 60 – 80 %. The main player in the Sri Lankan mining space is Lanka Mineral Sands Ltd, which is a fully owned government company. Governed under the Ministry of State Resources and Enterprise Development, the functions of the company are to mine, upgrade and export Sri Lanka's heavy mineral beach sands and primarily ilmenite, rutile and zircon are mined. Currently, Sri Lanka produces approximately 90,000 tons of Ilmenite, 9,000 tons of rutile and 5,500 tons of zircon annually ("Lanka Mineral Sands," 2017). As of 2016 records, Lanka Mineral Sands generated US$ 13,261,641 of foreign revenue from the sale of ilmenite, rutile and zircon to overseas parties.

Unfortunately, despite having several key deposits Sri Lanka is still behind in terms of adding value to the black sand. Value addition is further hampered due to an unsupportive political environment and local infrastructure towards manufacturing. Therefore, with focused scientific attention and careful economic planning much needed foreign exchange could be brought back to the country by exploiting long neglected treasure of black sand.

Sri Lanka's black sand is NOT a mirage!!!

References

1. TZ Minerals International. (2017). TiO2 Market Insight. Burswood
2. Lanka Mineral Sands. (2017). Retrieved October 23, 2017, from http://www.lankamineralsands.com/

***Professor Kottegoda** obtained her Bachelor's Degree in Chemistry from the University of Peradeniya and her Ph.D. in Material Chemistry from the University of Cambridge, UK. She is a Professor in Chemistry and is currently the Head of the Department of Chemistry at the University of Sri Jayewardenepura. She has contributed significantly in the field of smart agriculture through her groundbreaking innovation "Nano-urea fertilizer" which was seen to improve the efficacy of the current global agricultural output and was a means of adding value to commercially important natural minerals. Her pioneering research work on Nano-urea fertilizer has been highlighted as the "Global First" and the innovation has been awarded three US patents which were extended to six other countries.*

Mining Graphite for Graphene: The research that opened up opportunities

Dilushan R Jayasundara

Department of Physics, University of Colombo

Sri Lanka has a longstanding reputation for its high quality crystalline vein graphite with purity levels ranging well above 90% of carbon. It is a form of graphite mined as lumps and has highest degree of crystallinity, electrical and thermal conductivities, and cohesive energy of all natural graphite materials. Mining for graphite in Sri Lanka has over 200 year history and peaked during the world wars that resulted in significant revenue earnings. Recently resurgence in demand for graphite is observed and is anticipated to grow at an annual compound rate of 6.3 % in the years 2019 to 2025 (Adroit Market Research). This is largely owing to emerging applications and green initiatives in nuclear energy, fuel cells, semi-conductors and Li-ion battery technologies. For the existing graphite industry in Sri Lanka, this only means increase in mining and basic value addition in the form of purification. This is evident with most major graphite mines mining deep into the ore. However, rarely it has seen value addition in the form that both significantly increase its revenue generation per gram while preserving the resource into the future.

In 2010 the Nobel price wining invention of graphene, an atomically flat layer of graphite with exceptional physicochemical and electrical properties, lead to an increase in the interest of graphite among the scientific community. This transcended to industry interest with the expectation of top down chemical approach to produce graphene in large scale with properties appropriate for specific applications. For Sri Lanka to gain significant economic benefit through this chemical conversion process it requires a novel approach away from existing patented chemical synthesis methods. This requires fundamental understanding of the mechanistic details of chemistry behind the conversion of graphite to graphene. This was achieved through a systematic study on the evolution of oxygen functionalities during oxidation of graphite. The above understanding lead to the development of a novel synthesis process which only require H_2SO_4 and $KMnO_4$. With this new method it is possible to produce high quality large area single and few layer GO sheets as well as rGO, which is the reduced form of GO, that has exceptional thermal stability over a wide range of temperatures.

With a yield of approximately four times this new patented GO synthesis process, which is licensed, is expected to produce significant value addition to otherwise purified and exported graphite. While, challenges still remain in controlling the consistency of these synthesized graphene for large scale applications such as sensors, photovaltics, and energy storage devices the above invention has generated significant interest among Sri Lankan scientists to further develop the technology addressing these shortcomings. It is noted that technologies other than chemical processes are also now being explored to produce value added graphite-based products to accommodate demand for advanced devices. Furthermore, an increase in interest among local industries to incorporate graphene and its derivatives as part of value addition for their own products has been observed. This will lead to creating a demand within the country for value added graphite products. Thus it is possible to state that the expectations are high where graphite in the future will be mined to produce graphene.

Dr. Jayasundara *obtained his Ph.D. in physics from the University of Houston, USA and then joined Trinity College, Dublin as a postdoctoral fellow. He is currently a senior lecturer in the Department of Physics at the University of Colombo and a visiting researcher at Trinity College Dublin. He has also held the position of Senior Research Scientist at the Sri Lanka Institute of Nanotechnology (SLINTEC). His research interests include surface and interface physics and chemistry, functional coatings, surface functionalization, chemical and gas sensing, developing materials for water purification, and industrial quality control through NDT methods.*

Remarkable Inventions are already Exising in Nature; yet man should reveal

Rangika Halwathura

Department of Civil Engineering, University of Moratuwa

Nature is a huge teaching space that offers many lessons for those who take the time to reflect and discover. Scientists and inventors study characteristics of things in nature and come up amazing technologies and products invented as a result of studying nature. An emphasis toward more advanced admissions to building materials and life cycle performance continues to gain momentum to the whole impression of sustainable design. Sustainable building practice assays to identify how the built environment collides with the natural world and subsequently offers a balance with environmental veracity. However, instead of looking forward consider looking backward and analyze methods and technologies that were existed and used by our ancestors for their building industry can be a grand saving in environmental impact. Starting from sunbaked brick and to using earth as the primary building material. Further, it was found mud can be developed as a sustainable building material or use as raw material for building blocks. Then again mud has this greater weakness of decreasing the strength from time to time. In order to abolish this dandier impuissance, mud was combined with some possible binder materials and produced new building material call Mud Concrete(MC) and Mud Concrete Block (MCB). MCB (Sri Lankan Patent 17616-04| 2016) is again a result of cloning both past and modern construction technologies. This was then further investigated with other possible industrial waste products. Fly Ash, as an alternative stabilizer got the attention due to many reasons. Fly ash has some cementitious properties including its chemical composition. Cement chemical composition is Calcium oxide (lime), Silicon dioxide (silica), Aluminum oxide (alumina), Iron oxide and Sulphur. Similarly, Fly Ash also has a similar chemical composition such as Silicon dioxide (silica), Aluminum oxide (alumina). And also, the prevalent mineral in the clay/mud is Kaolinite. Kaolinite has very high-water absorptive capacity. It's an engineering problem which could be resolved by adding fly ash. Finally this led to another novel walling material, Geopolymerized Mud Concrete.

Plants are fascinating biochemists' man is able to attain from them a wondrous assortment of industrial chemicals. Both past and present Farming cultures of the world have intentionally improved the soils on which they planted. In the past, people have practiced in utilizing natural treatment technics to overcome their challenges. The use of plants parts for different purposes has been with man from the beginning mean time the technologies evolved. Studies of the chemistry of environmental enclosures provide critical evidence that can strengthen and augment interpretations based on its chemical analysis. Around 7000 B.C since mankind started cultivating, they had devised technics and practices on preventing the crops destroying by natural disasters as well as remarkably from insects. They were adopted selecting naturally resistant plants. Natural polymers have been tested for soil stabilization since prehistoric age. Natural Polymers were extracted from plants and trees. Compressive strength was subjected to understand the initial performance of each natural polymer.

In Sri Lanka, timber species have become popular for various applications and functions based on its unique characteristics. The growth of the Wood Preservation Industry has been one of the most important technical developments within the forest industry. The wide acceptance of preservation as an integral part of wood processing and utilization has been a significant contribution to the use of what is the only structural raw material having a renewable and sustainable source of supply. There are timber structures still in existence after hundreds of years of service. Essentially, the science of wood preservation is the treatment of wood to increase durability and give extended service life. This involves the placement, within the wood microstructure, of preservative chemicals which are antagonistic to wood destroying agencies. A rich heritage of knowledge on preventive was available in ancient knowledge and practice in Sri Lanka. Most pesticides contain other elements. Among them Chlorine, oxygen, sulfur, phosphorus, nitrogen, and bromine are most common.

Inert ingredients can be many substances, dependent on the type of pesticide. Pesticides are by their very nature toxic substances. Plant-based natural constituents can be derived from any part of the plant like bark, leaves, flowers, roots, fruits, seeds and so on, that is any part of the plant may contain active components.

Sustainability has become the most important challenge for the building and construction industry, not just for the present, but also for the decades to come. Scientifically-based solutions should drive technological innovations that enable compliance with the still-growing environmental constraints. Research in this particular field of interest is advanced from the physical, chemical, biological, lifecycle assessment, engineering, and materials science perspective, often leading to synergistic approaches.

***Prof. Halwatura** obtained his Ph.D. in Structural and Building Services Engineering from the University of Moratuwa, Sri Lanka in 2008. He is currently a Professor in the Department of Civil Engineering, at the University of Moratuwa, a chartered engineer from the Institution of Engineers and an Associate Member of the Society of Structural Engineers. Prof. Halwatura is an editor and reviewer of multiple journals and his research interests lie in the fields of Sustainable material and design, Green technology, Construction Management, Structural Designing, Project Planning, and Monitoring, Computer-Aided Server Based Project planning and Monitoring, Forensic Engineering, and BIM (Building Information Modeling).*

Conference Proceedings

Exploring strategies for the value addition of herbal products in Sri Lanka

Priyani Paranagama

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Despite its small size, the differences in climate, topography and the existence of coastal areas have made Sri Lanka one of the most biologically diverse countries in the world. With about 20% of its area covered in forests and over 3000 indigenous species recorded, Sri Lanka is also known to have the highest species diversity per unit area in Asia. For many years, people have used medicinal and aromatic plant species due to their curative and aesthetic potential. Plant material based products constitute a significant percentage of the global market, with about 50% of the population being dependent on them. The value addition of a commodity becomes a necessity if a country is to commercially exploit its natural resources and create marketable products. Most of the time, even an authentic plant species tend to get rejected because it does not have the desired active compounds or strength to match the pharmacopoeia standards and the requirements of the industry. Though initially, value addition to natural products was done by trial and error methods and with experience gained over years of using them, the advent of state-of- the-art technology has made the effective isolation and identification of chemical compounds responsible for enhancing human physiology much easier. Discoveries have been made that enabled different parts of the same plant to be used for treating an ailment, for adding flavor and incorporating fragrance. For example, the stem bark of *Cinnamomum zylanicum*, commonly termed Ceylon cinnamon, can be used to extract the essential oil with cinnamaldehyde while its leaves can be used to extract the essential oil with eugenol. Exported commodities from Sri Lanka include orthodox Ayurvedic products that are used to impart therapeutic value to food and essential oils that are used in cosmetics. The conservation and rational use of medicinal plant species in Sri Lanka has been a concern and several initiatives have been taken by the relevant authorities in this regard. There are regulations to manage the quality and safety of the supply and value chain of consumer products and also schemes to support companies to obtain direct information on novel products, services, and technologies that are used internationally. However, there are many challenges that Sri Lanka needs to overcome if it is to gain a competitive advantage in the global market. Unfortunately, most of the countries with much fewer resources have a bigger market share of the natural product economy than Sri Lanka. Eventhough major medical breakthroughs have been made by using the medicinal power of plants, their therapeutic aspect and mode of action are yet to be explored. Lack of funding together with the absence of advanced experimental and standardization procedures has made Sri Lanka fall backward. If Sri Lanka is to secure a worthy place in the herbal product market, we have to come out of the shell and implement good manufacturing and laboratory practices to our production lines whilst making fruitful collaborations and focusing on multidisciplinary research work with developed countries.

***Professor Paranagama** obtained her bachelor's degree in Chemistry from the University of Kelaniya in 1986, M.Phil. degree in Organic Chemistry in 1991 and her Ph.D. from the University of Glasgow in the field of Bio-Organic Chemistry. Currently, she serves as the President of the Institute of Chemistry Ceylon, Director of the Institute of Indigenous Medicine, and Senior Professor at the University of Kelaniya. She has served as the Dean of the College of Chemical Sciences, and as the Head of the Department of Chemistry, at the University of Kelaniya. She is a fellow of the Institute of Chemistry Ceylon and a Chartered Chemist from the Royal Society of Chemistry. Her research interests include isolation and characterization of bioactive natural products from plants and endolichenic fungi, development of bio pesticides and the value addition of natural products.*

Conference Proceedings

Value addition by innovative polymer modifications

K M Thilini D Gunasekara

Department of Chemistry, University of Sri Jayewardenepura

The field of polymer is generally represented by rubber, plastic, fibers, and adhesives. Polymers which have been used to be cheap substitutes for day to day applications have transformed into indispensable materials providing high-quality constituents for a wide variety of sophisticated applications. Polymers are now produced in great quantity and variety. Each and every day we depend so much on polymer products that without them we would not be able to live in our civilized world. Since the consumption of polymeric products increased every day, it is expected to experience an explosion of polymer utilizations in coming years. Thus, further advances and breakthroughs in the field of polymer must be encouraged by any nation which may could strongly contribute the national economy in the coming years.

Value addition is one such endeavor the Sri Lankan polymer industry may contemplate. It is the enhancement of the raw material, or product which can be considered as the addition of an extra special feature by a producer to increase the value of a product. Value addition by polymer modifications opens up pathways for innumerable industrial applications. The process of polymer modification could be envisioned to attribute different yet desired properties to the properties of the materials such as imparted conductivity, enhanced thermal stability, biodegradability, multiple physical/ chemical responses, etc. On that note these polymer modifications can be considered as physical modifications and chemical modifications.

Entanglement and entrapment can be considered as physical modification. Development of conducting rubber is one such spectacular unique physically modification of rubber. Rubber is a class of materials traditionally established as insulators. However, by the entrapment of conductive additives like carbon black, carbon fiber, metal, or metal oxide, none conducting rubber can convert to conducting material. Since Sri Lanka is blessed with best graphite in the world as well as Sri Lanka is among the ten prestigious worlds Natural Rubber produces offering different types, forms and grades and the supplier of the best crepe rubber, it would be a winning combination of both industries if a conducting rubber could be developed by physically modifying rubber with graphite.

Sri Lanka is not blessed to have natural resources of plastics. Nevertheless, many creative modifications could be done on virgin plastics. Super-hydrophilicity or super-hydrophobicity could impart on plastics by simply incorporating necessary additives. Smart fibers/textile materials could design by adding stimuli sensitive functionalities to the plastics through chemical modifications. As one may state as cutting edge science, self-healing materials may also acquire by identifying and chemically modifying the appropriate functional groups of a plastics. Creative solutions can be established for plastic degradability by either chemical or physical modifications of plastics. Further, plastic trash may convert into valuable other materials with the combination of creativity and physical/chemical modifications of plastic trash.

If one looks at the Sri Lankan Polymer industry, value addition did had taken place in a considerable manner, yet more space and areas left for the improvement and further developments. Nevertheless, innovative polymer modifications would be a tangible and attractive effort in uplifting our nation's economy.

***Dr. Thilini Gunasekara** obtained her Ph.D. in photochemistry from Bowling Green State University, Ohio, USA in 2008. She worked as a post-doctoral fellow at the Spectra Group Ltd USA and at Petroleum & Geosystems Engineering, University of Texas. Currently, she is the Head of the Department of Polymer Science and the Director of the Center for Advanced Material Research at the University of Sri Jayawardanapura. Dr. Thilini is also the Immediate past president of the Environment committee of the SLAAS and the Toastmasters club of the University of Sri Jayawardanapura. Her research interests include the design and development of smart material and hydrogels, that find remarkable use in water purification and in medicine.*

Conference Proceedings

Value added biochar for a sustainable environment

Sameera R Gunatilake

College of Chemical Sciences, Institute of Chemistry Ceylon

Biochar (BC) is produced by the thermochemical conversion of biomass under anaerobic conditions. The resulting cost-effective carbonaceous adsorbent is utilized extensively due to its pollution remediation and agricultural soil amendment capabilities. Also, BC production allows solid waste management and carbon sequestration. There can be numerous chemisorptive and physisorptive mechanisms responsible for BC-adsorbate interactions which depend on the surface characteristics of BC such as the porous structure, surface functionality, and charge. The aforementioned characteristics depend on its feedstock type (FS), production conditions, and any physical and chemical value additions. The value addition of BC, which can be carried out as pre- or post-modifications, can either enhance or ease the sorption process. Enhanced adsorption capacity can be due to pore wall destruction, oxidation of surface functional groups and removal of minerals whereas magnetization leads to an easy recovery process. Furthermore, higher adsorption efficiencies can be achieved by providing optimum conditions of pH, contact time, etc. Focuses of this presentation are on correlating the effect of different FSs, pyrolysis conditions, value additions, adsorption capacities, and digestion methods with the performance of BC.

Nitric, sulphuric and hydrochloric acid modifications were carried out on tea waste biochar (TWBC) produced under three different pyrolysis conditions, 300, 500 and 700 °C, in order to evaluate how the physicochemical properties of the BC were influenced. Changes to the surface morphology and functionality, point of zero charge, cation exchange capacity (CEC), thermal stability, and ultimate and proximate analysis of both raw and modified BC were compared. The low temperature produced BC which had the highest CEC was seen to further increase upon nitric acid modification as a result of the 81.89 % increase in carboxylic functionalities. Slow pyrolyzed TWBC was utilized in studying the adsorption of Pb and Cd as well. The best performance was observed by the BC produced at 500 °C where the observed capacities for Pb and Cd were 57.8 and ~29.0 mg/g respectively. When the raw BC was magnetically modified, the adsorption capacities of Pb decreased by 15.9 %. The increased capacities of Cd by 32.75 % was due to the cationic π bonding interaction between the iron oxides and the cationic metal species. Magnetized Douglas fir BC was used to study the adsorption capacities of PO_4^{3-} and As(III). The capacities observed were 90 and 5.49 mg/g respectively, which was attributed to chemisorptive interactions that took place mainly by H bonding. Municipal solid waste BC was used for the remediation of toluene and xylene whilst acting as a means of solid waste management. Biochar produced at 300 °C using Lasia Spinosa (kohila) showed the highest capacity in a methylene blue adsorption study. The capacity was seen to further enhance by more than five times after a nitric acid premodification due to pore widening. A novel digestion method was optimized for nine different BCs where the desired dissolution of the solid matrix and matrix interference was obtained by using fuming nitric acid (98%).

***Dr. Sameera R Gunatilake** graduated from the Institute of Chemistry Ceylon in 2007 and obtained his Ph.D. in Analytical Chemistry from the Mississippi State University in 2014. He is currently serving as a senior lecturer at the College of Chemical Sciences and is the Honorary Editor of the Institute. He is also a council member at the Sri Lanka Academy of Young Scientist (SLAYS). His research interests encompass the development of an engineered low-cost adsorbent for water remediation and as an agricultural soil amendment.*

Conference Proceedings

Organic Synthesis on Graphene and other carbonaceous Materials

Laksiri Weerasinghe
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Carbon is widely available inexpensive material. Graphene is a two-dimensional crystalline carbon allotrope that has fascinated researchers worldwide and has extended the interest in carbon structures such as fullerenes and nanotubes Carbon-based-materials have been utilized for a variety of applications including organic synthesis and heterogeneous catalysis. Various carbonaceous materials have been used as alternatives for transition metal based catalysts. These carbon based materials have shown their potential for development of green and sustainable approaches to heterogeneous catalysis. In this presentation, the utilization of carbon-based materials as supports for heterogeneous catalysts, especially in organic transformations will be discussed. Predominantly on four categories of carbonaceous supports, namely graphene (including, graphene oxide (GO) and reduced graphene oxide (rGO), graphitic carbon nitride (GCN), carbon nanotubes (CNT) and activated carbon (AC) for various organic reactions will be discussed. Several approaches for the synthesis of these materials along with their application as heterogeneous catalysts for organic reactions will be elaborated in detail. In addition, different aspects of organic synthesis, including hydrogenation, oxidation, reduction, condensation, and multi-component reactions, catalyzed by these materials will also be discussed along with the organic transformations leading to the sustainable synthesis of valuable products from biomass. The future perspectives of this very interesting class of materials will also be provided.

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Cover Page

The picture illustrating the theme "**Advances in Electrochemical Technology**" was adapted from the "To boost Lithium – Ion Battery Capacity by up to 70%, Add Silicon" article by David Schneider which appeared in the IEEE Spectrum website on 6th January 2019 which discusses about Silicon rich anodes will let batteries hold more energy. This article can be found using this URL https://spectrum.ieee.org/energy/renewables/to-boost-lithiumion-battery-capacity-by-up-to-70-add-silicon

Guest Editorial

A Breakthrough in Battery Research: Lithium Ion Batteries

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As the energy crisis is growing, the need of having a sustainable energy economy has become crucial more than ever to cope with the high energy dependence and demand of the modern day-to-day work. Development of cost effective and efficient advanced electrical energy storage systems plays a critical role in ensuring the clean, sustainable, and secure energy supply. At present, lithium ion batteries (LIBs) power most of the portable electronic devices. LIBs have higher specific energy, energy density, and specific power compared to the other energy storage technologies and therefore preferred for energy storage applications. Figure 1 is a Ragone plot of specific power vs specific energy variation and it demonstrates that LIBs have greater specific power and specific energy compared to the other battery technologies [1]. It is anticipated that LIBs will also dominate in applications like transportation and stationary electricity storage in the future. Even currently, LIBs dominate and own 37% revenue share, which is the highest percentage compared to other battery technologies. In 2018, annual worldwide LIB production was estimated to be USD 29.27 billion. By 2026, the market value is expected to reach USD 95.89 billion, growing at a CAGR of 16.4% during the forecast period [2].

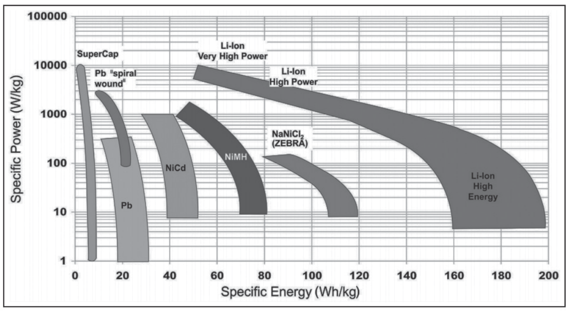

Figure 1. Ragone plot of different battery technologies. SuperCap: supercapacitor; Pb: lead; Li-ion: lithium-ion; NiCd: nickel–cadmium; NiMH: nickel–metal hydride; NaNiCl2: sodium–nickel chloride; ZEBRA: Zero Emission Battery Research Activities.[1]

Lithium:

Prior to invention of LIBs, the existing battery technologies suffered from limited energy density, low capacity, and low voltage. Researchers were trying to develop better battery materials and lithium was considered due to its favorable properties to serve as an excellent battery element. Lithium is the lightest metal, with an atomic mass of 6.941 g mol^{-1} and a density of only 0.53 g cm^{-3}. Theoretical capacity of lithium is 3861 Ah kg^{-1}. Lithium also has a significantly low standard reduction potential (-3.05 V vs SHE for Li^+/Li). These properties makes lithium an excellent candidate for high energy dense, high capacity, and high voltage battery chemistry.

Basic structure:

As in any electrochemical system, LIB comprises of a negative electrode (referred as anode) and a positive electrode (referred as cathode) which are connected through an electrical circuit. In a conventional LIB, a graphite anode and a lithiated transition metal oxide (LTMO) cathode are used. There are five main types of commercialized LTMOs used in LIBs. Lithium cobalt oxide ($LiCoO_2$, LCO), lithium manganese oxide ($LiMn_2O_4$, LMO), lithium nickel manganese cobalt oxide ($LiNiMnCoO_2$, NMC), lithium iron phosphate ($LiFePO_4$, LFP), and lithium nickel cobalt aluminum oxide ($LiNiCoAlO_2$, NCA) are the five main types of LTMOs used to date in LIBs [3]. Figure 2 is a diagram of the LIB. Anode and cathode are placed in an electrolyte medium. Typically, electrolyte is a mixture of organic carbonates (eg: ethylene carbonate, diethyl carbonate) containing a salt of lithium (eg: lithium hexafluorophosphate, lithium perchlorate, lithium triflate). Battery separators provide a barrier between the anode and the cathode while enabling the exchange of lithium ions from one side to the other. Usually, polyethylene or polypropylene separators are used in LIBs.

Function:

The half reactions take place at the anode and the cathode during discharge are given in Equation (1) and (2) respectively. The cathode discharge half reaction in Equation (2) is given considering LCO as the electrode material. The overall discharge reaction is given in Equation (3), and the reverse reaction takes place during the charging process. During the discharge process, intercalated Li in graphite anode are oxidized to Li^+, and deintercalated to the electrolyte medium. At the cathode, Li^+ are reduced to Li and intercalated in CoO_2. Oxidation and reduction reactions drive the intercalation and deintercalation processes. Figure 2 illustrates the discharge process.

During discharge:

Anode half reaction anode:

$$LiC_6(s) \rightleftharpoons Li^+(aq) + C_6(s) + e \qquad (1)$$

Cathode half reaction cathode:

$$Li^+(aq) + CoO_2(s) + e \rightleftharpoons LiCoO_2(s) \qquad (2)$$

Overall reaction:

$$LiC_6(s) + CoO_2(s) \rightleftharpoons C_6(s) + LiCoO_2(s)$$

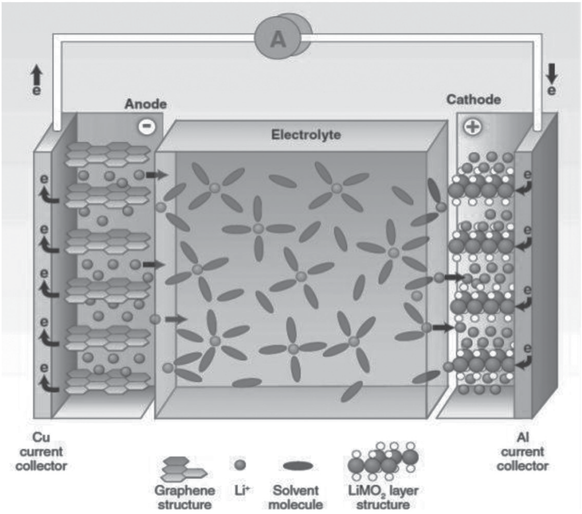

Figure 2. Diagram of the lithium ion battery. Process during the discharge is indicated in the diagram.[4]

Intercalation Chemistry

Intercalation/deintercalation is one of the major mechanisms takes place in LIBs to store energy. Intercalation means incorporation of guest species such as atoms, ions, or molecules, into a host crystal lattice, without destroying host lattice structure. Two main conditions must be satisfied to achieve successful lithium intercalation/deintercalation with a host structure [5]. (1) The host compound must be crystalline. Also, there must be empty sites in the form of isolated vacancies or 1D channels, 2D layers, or 3D network channels. (2) The host compound must contain a transition metal or rare earth metal which can exhibit one or more stable valency states.

Compounds with vacancies are needed to accommodate lithium. Compounds with isolated vacancies or 1D channels may intercalated easily but they are hard to deintercalate. Therefore, in compounds with 2D or 3D vacancies lithium intercalation/deintercalation is more feasible. When lithium is intercalated, lithium ion is intercalated along with the electron. Intercalation reduces the valency state of the host compound by one unit and the compound should be able to accept the electron. Compounds without one or more stable valency states are not suitable for intercalation.

Lithium metal anode

Initial cell configuration used lithium metal as the anode material. When using lithium metal as the anode, dendrite formation was a huge problem. Upon repeated charge-discharge cycles, lithium metal was plated on anode. These dendrites could be large enough to go through the separator and reach the cathode. When lithium metal dendrites reach and contact with cathode, it causes short circuiting and start a thermal run-away reaction on the cathode. This causes the battery to catch fire. Li metal also suffers from poor cycle life. Due to these reasons, lithium metal anode was avoided during the LIB development. As an alternative, carbonaceous anode material were considered.

Anode material

A material should exhibit following properties to be used as an ideal anode material in rechargeable LIBs [5]. (1) Material should have elements/compounds with low atomic/formula weights and it should have low density. (2) Material should possess the ability to accommodate significantly large amount of Li per formula weight. (3) Material should be cyclable to result large, stable, and reversible gravimetric and volumetric capacities. (4)

The potential of the material should be low with respect to Li, i.e. potential should be close to that of Li. Also, upon lithiation-delithiation, the material should not show significant variations in the potential. (5) Material should be insoluble in the solvents and behave inert with solvents and electrolytes. (6) Material should have excellent electronic and Li ionic conductivity. (7) The material should be inexpensive. (8) The material should be environmentally friendly.

Most common anode material used in LIBs is graphite. Graphite can intercalate Li atoms to form LiC_6, a stage 1 intercalation product, resulting a theoretical gravimetric capacity of 372 mAh g^{-1}. Graphite has a low potential of 0.15 – 0.25 V vs Li. Due to a chemical reaction takes place between Li and solvent, a protective layer called solid electrolyte interphase (SEI) is formed on the external surface of the graphite particles during the first few charge-discharge cycles. SEI has several advantages. SEI prevents cointercalation of solvent, acts as a good Li ion conductor, enables facile cycling, and protects reducing agent, charged graphite (LiC6), from unwanted side reactions. Graphite is a semiconductor and has a conductivity ($\sigma_{300\,K}$) of 10^{-2} – 10^{-3} S cm^{-1}. Charged graphite (LiC_6) has a metallic-type conductivity ($\sigma_{300\,K}$) of 10^{2} – 10^{3} S cm^{-1} and a high Li ion diffusion coefficient (DLi^+ at 300 K) of 10^{-8} – 10^{-10} cm^2 s^{-1}.

In addition to graphite, lithium titanate oxide (LTO), conversion anode Type A, and conversion anode Type B (eg. Si) are studied as potential anode material for LIBs.

Cathode Material

There are key requirements a material should fulfill to be used as a suitable cathode material in a rechargeable battery [6]. (1) The material should have a readily reducible and oxidizable ion. (2) Material should react with lithium in a reversible way preferably via intercalation-deintercalation. There should not be co-intercalation of the electrolyte ions. (3) The reaction between material and lithium should have a high free energy, i.e. high capacity and high voltage, which lead to a high energy density. (4) The reaction between material and lithium should be very fast which leads to a high power density. (5) The material should be a good electrical conductor which leads to easy oxidation and reduction during the electrochemical reaction. (6) The material should be stable, i.e. should not degrade or should not change the structure upon intercalation-deintercalation. (7) The material should be inexpensive. (8) The material should be environmentally friendly.

There are mainly two types of cathode materials [6]. The first category is the layered compounds with an anion close-packed lattice. The alternate layers between anions sheets are occupied with a redox active transition metal cation. Lithium can insert into the remaining empty layers. Examples for the first structure type are LCO, NMC, and NCA. Spinels are a special group of material, where the transition metal cations are arranged in all the layers. LMO has a spinel structure. The second category have more open structures. LFP is an example for the second structure type. Due to the compact structures, the main advantage of the first type is having a high energy density. The main advantage of the second structure type is the lower cost. A comparison of the basic properties of the five main commercialized cathode materials are listed in Table 1 [7].

In addition to above mentioned intercalation cathode materials, conversion cathode materials like metal fluorides, metal chlorides, selenium, and tellurium are studied as potential candidates.

Future of lithium battery

Improving LIBs further for high power high and

Table 1. A comparison of the basic properties of the five main commercialized cathode materials [7].

Compound	Specific capacity (mA h g^{-1})		Volumetric capacity (mA h cm^{-3})		Average voltage (V)
	Theoretical	Practical	Theoretical	Practical	
LCO	274	148/145	1363	550	3.8
NMC	280	160/170	1333	600	3.7
NCA	279	199/200	1284	700	3.7
LMO	148	120	596	--	4.1
LFP	170	165	589	--	3.4

energy density applications is the main objective of the current research. To achieve the objective, four critical criteria should be fulfilled [5]. (1) Cost reduction. For the cost reduction, cheaper electrode and electrolyte material needed to be found as these account for about 40% of the cost. (2) Improvements in the energy density. The energy density depends on the capacity and operating voltage of the electrode material. Currently, the practical capacities are less than the theoretical capacities. Electrode materials with higher capacities, as well as electrode materials that can utilize most of the theoretical capacity should be developed. Also, cathode materials with high operating potentials and anode materials with low operating potentials are preferred. Energy densities are expected to improve from about 120 W h kg^{-1} to 250 W h kg^{-1}. (3) Safety in operation. Safety issues occur due to overcharging or over discharging. The devices can catch fire or evolve smoke. This can be due to charged anode/cathode which are thermally unstable and powerful reducing/oxidizing agents coming into contact with electrolyte or dendrite formation. Presence of a sophisticated safety electronic circuit will prevent overcharging and discharging problems. The other most crucial aspect is the heat management. Like other electrical energy systems, about 15% of the energy is lost as heat. In larger systems with LIBs, explosions can take place if the precautions are not taken. (4) Improvements in the low and high temperature operations. At low and high temperature operation capacity fades. It is anticipated to improve the temperature limits to 0-10 °C from low end and 60-80 °C from high end.

Making history: Nobel Prize in Chemistry 2019

Invention of the LIB is a breakthrough in battery research. Currently, LIBs are the most widely used rechargeable battery type. John B. Goodenough, M. Stanley Whittingham, and Akira Yoshino were jointly awarded the Nobel Prize in Chemistry 2019 "for the development of lithium ion batteries". Figure 3 shows the graphic of the three Nobel laureates from the official website of the Nobel Prize. Individual work carried out by these researchers became collectively critical to develop the LIB technology. In 1970s, Whittingham developed a battery with a titanium disulfide cathode and a lithium metal anode. Titanium disulfide functioned via intercalation-deintercalation chemistry. Voltage of the battery was around 2 V, but, the use of metal lithium caused safety issues. In 1980s, Goodenough developed a battery with a remarkable cathode material, lithium cobalt oxide (LCO). This material could double the battery voltage. However, still lithium metal was used as the anode. In 1990s, Yoshino was investigating alternative anode material for lithium metal. He replaced lithium metal with petroleum coke, a by-product from oil industry. LCO was used as the cathode. He was able to develop a safe battery chemistry based on intercalation and deintercalation while not compromising the battery voltage. This lead to the commercialization of safe, high energy dense, high voltage lithium ion batteries in 1991.

Ill. Niklas Elmehed. © Nobel Media.
John B. Goodenough
Prize share: 1/3

Ill. Niklas Elmehed. © Nobel Media.
M. Stanley Whittingham
Prize share: 1/3

Ill. Niklas Elmehed. © Nobel Media.
Akira Yoshino
Prize share: 1/3

Figure 3. John B. Goodenough, M. Stanley Whittingham, and Akira Yoshino were jointly awarded the Nobel Prize in Chemistry 2019 "for the development of lithium ion batteries".[8]

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Themed Collection : Advances in Electrochemical Technology

Themed Collection

Electrochemical Energy Storage: Supercapacitors

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Various technologies are operated to supply the energy demands such as fossil fuels, nuclear energy, and renewable energy sources. Fossil fuels are depleting at an alarming rate emphasizing the need of alternative greener energy sources like solar and wind. The discrepancy between peak supply and demand from energy sources like solar and wind intensifies the necessity of high-performance energy storage systems.

Batteries possess high energy density with low power density whereas conventional capacitors exhibit high power with lower energy density. Supercapacitors also known as ultracapacitors possess a balance of energy and power densities which bridge the gap between conventional capacitors and batteries. Supercapacitors are capable of delivering more power than batteries and store higher energy density than conventional capacitors. This nature of electrochemical performance of supercapacitors makes them for many useful application like alternative energy industries, transportation, electronics, and communication.

Increasing the energy density of supercapacitors while maintaining the other fascinating properties has become an emerging field of research on energy storage. Depending on the energy storage mechanism they possess, supercapacitors can be classified in to two major categories, as pseudocapacitors and electrochemical double layer capacitors (EDLCs). Pseudocapacitors store energy by fast oxidation reduction reactions between electrode material and electrolyte ions.[1] Although this mechanism yields higher energy density it suffers from poor cycling stability and low conductivity, which hinder it the usability of pseudocapacitors in real world applications. On the other hand EDLCs store energy through pure electrostatic charges accumulated at the electrode/electrolyte interface. Since the EDLCs have electrostatic mechanism it can rapidly release charges, while maintaining exceptional cycle life. Electrochemical performance of supercapacitors depends upon the specific surface area, pore size distribution, and conductivity of the electrode material.

Capacitance (C) is the charge (Q) per unit voltage (V) which is shown in equation 1.1.

$$Q=CV \qquad 1.1$$

$$C = \varepsilon_o \varepsilon_r \frac{A}{d} \qquad 1.2$$

Capacitance related to the geometry of electrode which can be expressed as equation 1.2, where ε_r, dielectric constant of the electrolyte, ε_0, dielectric constant of vacuum, d is the thickness of the double layer.[1] EDLCs, as the name imply two electrodes make two double layers upon charging, which represents a combination of two capacitors in series and the capacitance can be shown by equation 1.3.

$$\frac{1}{C_T} = \frac{1}{C_1} + \frac{1}{C_2} \qquad 1.3$$

The energy density and power density of a supercapacitor expressed in equation 1.4 and 1.5.

$$E = \frac{1}{2} CV^2 \qquad 1.4$$

$$P = \frac{V^2}{R_S} \qquad 1.5$$

Capacitance is directly proportional to surface area and inversely proportional to the thickness of the double layer. Increasing the capacitance enhances the overall electrochemical performance of supercapacitor. The distance between double layer is several Angstroms apart, which is at a minimum level. Therefore, increasing the surface area of electrode is a vital technique to enhance the capacitance, and hence the overall electrochemical performance.

EDLCs primarily utilize carbon materials as electrodes. Variety of carbons such as carbon nanofibers (CNFs), carbon nanotubes (CNTs), carbon aerogels (CAGs), mesoporous carbon,[2] and graphene have been explored as electrode materials. Surface area of the carbons can be increased upon activation at high temperatures. Activation is a widely used technique to increase the surface area. Activated carbons considered as highly porous, which contain micro (< 2 nm), meso (2-50 nm), and macro (> 50 nm) pores. These pore architectures involved as ion buffering reservoirs, decreasing ion transport resistance, and absorbing electrolyte ions to form the double layer.[3]

On the other hand CNFs possess superior properties such as high surface area, high mechanical strength, flexibility and relatively good conductivity. Due to these properties CNFs are a promising candidate for supercapacitor electrode materials. CNFs can be derived from carbon containing polymers after electrospinning.

Electrospinning is a versatile technique to obtain fibers with a size range of nanometers to several microns. Basic electrospinning station consist of three main components; a high voltage source, a capillary spinneret, and a collector (grounded/oppositely charged). In brief the polymer solution is filled to a syringe and connected to a needle. Upon application of the voltage, the polymer solution makes a hemispherical shape at the needle tip which is known as a Taylor cone. At the point where the repulsive electrostatic force exceeds the threshold surface tension the polymer solution is drawn out as strands. These strands are deposited on the collector and make a non-woven fibrous mat. Electrospinning depends on several parameters such as the nature and characteristics of the polymer, solution properties (e.g. conductivity, viscosity, and surface tension), magnitude of the electric field, tip to collector distance, temperature, relative humidity, and needle gauge. The electrospun fiber mat is subjected to a heat treatment process in order to obtain carbon with better performance. There can be further heat treatments depending on the activation method used to obtain better surface area.

Recently novel 6FDA-based polymers were explored so that the amount of the in-situ porogen, DABA (diaminobenzoic acid) moiety is adjustable. 6FDA-DABA (100% DABA), 6FDD (6FDA-DAM:DABA 3:2) (40% DABA), and 6FDA-DAM (2,4,6-trimethyl-1,3-phenylenediamine) (0% DABA) were synthesized, electrospun and carbonized. Carbon fibers obtained from 6FDA-DABA and 6FDD displayed a specific capacitance of 89 Fg-1 whereas 6FDA-DAM exhibited essentially no capacitance upon carbonization. As expected, subsequent activation with CO_2 at 1000 °C increased the surface areas and electrochemical performance of all three family members with the 6FDA-DABA-derived fibers exhibiting the highest performance. 6FDA- DABA exhibited the best performance with specific capacitance of 147 Fg^{-1}, energy density of 66 $Whkg^{-1}$, power density of 3.4 $kWkg^{-1}$ with 96% capacitance retention after 3000 cycles and is a promising candidate for supercapacitor electrode material for high energy and power applications.[4]

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Bubble Nucleation-based Electrochemical Detection of Surfactants

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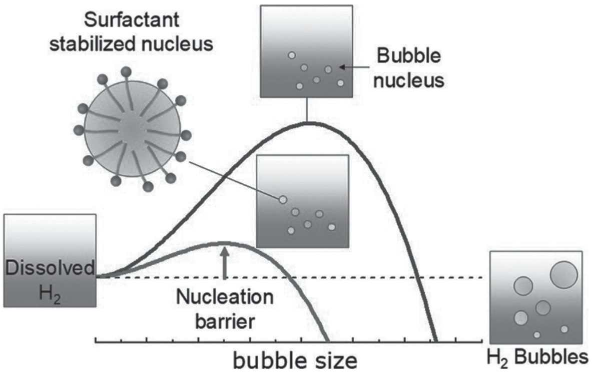
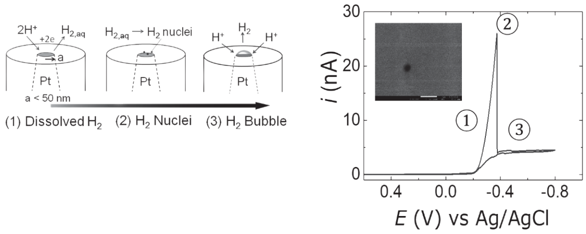
The formation and evolution of vapor and gas bubbles in a liquid body is a phenomenon of vast fundamental and applicative interest, for example, in commercial electrolytic processes in cavitation, in biomedical applications, and functional material fabrication.[1] Here, we present a new application of gas bubbles for surfactant detection. Our method is based on the interactions between gas nuclei and surfactant molecules during electrochemical gas bubble nucleation. According to classical nucleation theory (CNT), nucleation of a gas bubble requires a supersaturation of dissolved gas because of the energy barrier of establishing a new gas–liquid interface (Scheme 1). In the presence of surfactant molecules, gas nuclei can be stabilized because of the reduced surface tension of the gas–liquid interface, leading to a decrease of the supersaturation level required for bubble nucleation.[2] In our method, we take advantage of the high surface activity of surfactant analyte to affect the bubble nucleation and transduce the change in the supersaturation level required for bubble nucleation to electrochemical signal for highly sensitive and specific detection of surfactant analytes.



Scheme 1. Bubble-Nucleation-Based Electrochemical Method for Surfactant Detection

To electrochemically probe the bubble-nucleation condition, we adopted a nanoelectrode-based approach developed by Luo and White.[3] In this approach, a sub-50-nm Pt nanoelectrode is used to perform hydrogen evolution reaction (HER) in acid solutions. As the nanoelectrode potential is scanned negatively, the HER current increases exponentially until it reaches a peak value (ipeak). Past ipeak, the HER current immediately drops to a minimal value, which corresponds to the nucleation and formation of a gas bubble at the nanoelectrode, blocking the electrode surface (Scheme 2). The supersaturation level of dissolved H_2 gas required for H_2 bubble nucleation is proportional to the ipeak value.



Scheme 2. Peak current provides information regarding the bubble nucleation.

Perfluoroalkyl Substances (PS) are persistent and globally distributed environmental contaminants. Analytical methods used for PS detection are currently dominated by chromatography in combination with mass spectrometry. These methods are highly sensitive and selective but expensive (typically > \$100/sample) and unsuitable for low-cost, on-site screening. Our detection method takes advantage of the high surface activity of PS, which affects the electrochemical bubble nucleation, and then transduces the change of nucleation condition to electrochemical signal for PS quantitation. The nanoscale dimension of the electrodes provides exquisite sensitivity for detecting slight changes near or at the electrode surface, while fast electrochemical measurements allow studying the dynamics of bubble nucleation. When PS concentration increases, the solution surface tension decreases, resulting in a lower nucleation energy barrier. Consequently, a lower supersaturation concentration is required for H2 nanobubble nucleation resulting in a reduction of bubble nucleation current. Using this method, we demonstrate the quantitation of perfluorinated surfactants in water, with a remarkable limit of detection (LOD) down to 80 μg/L and a linear dynamic range of over three orders of magnitude. With the addition of a preconcentration step, we have achieved the LOD range covering 70 ng/L, the health advisory for perfluorooctane sulfonate and perfluorooctanoic acid in drinking water established by the US EPA. The experimental results are in quantitative agreement with the model we derived from classical nucleation theory. We further tested the specificity of this method for detecting surfactant analytes by adding an excess of nonsurfactant interference, polyethylene glycol (PEG, 400 g/mol), which has a similar molecular weight as PFOS. The addition of PEG leads to a negative shift of the HER onset potential as compared to the PFOS-only sample, but the ipeak does not show any notable difference. Apart from that, we have also tested different concentrations of humic acid and lysozyme. We observed no trend in the peak current compared to that of the blank. These results show the exceptional specificity of our method for surfactant analytes. This research provides the proof of principle study of a bubble nucleation-based sensing platform, which will be further developed toward a low-cost and portable tool for on-site detection of PS compounds in water. In addition, our method has the potential of further developing into a universal electrochemical detector for surfactant analysis due to its surface activity-based detection mechanism.

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Perovskites; Next Star Material for Clean Energy

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Photovoltaic Technology

One of the major challenges humanity must address is to transition away from a reliance on fossil fuels for energy production to clean, renewable sources of energy. There are three major motivations which drive research in renewable energy;

- Combatting the nonlinear climate changes that are occurring as a result of global warming, resulting from the significant emission of greenhouse gasses particularly CO_2 produced by burning of fossil fuels.
- The need to find sustainable and cost effective solutions to the depletion of conventional fossil fuel sources, since the demand for fossil fuels is predicted to increase dramatically with the growth of the global population.
- The need for many nations to improve energy security, which requires them to reduce dependence on other (less stable) nations for energy.

Energy generation from sunlight (both heat and electricity) is an ideal way to replace fossil fuel sources of energy in many situations, since the sunlight it is an abundant, clean and renewable source of energy: The energy in the sunlight incident on the Earth's surface in one hour is sufficient to meet the annual global energy demands. One of the major breakthroughs in modern science, which has attracted a great research interest is in the photovoltaic (PV), which are devices that convert sunlight directly into electricity without moving parts (except electrons!), noise or emissions. According to the International Energy Authority (IEA) it is predicted that by 2050, PVs will be the largest contributor to the global renewable energy landscape.

At present the commercial PV market is dominated by PVs based on conventional semiconductors, primarily silicon. However, there are drawbacks to silicon PVs technology, namely; (i) highly purity silicon is required, which is relatively expensive to produce; (ii) very high temperatures are required to process silicon because single crystal ingots are grown from melted silicon, thus leading to high energy outlay in production and long energy payback times; (iii) by comparison with other single junction PVs, silicon requires very thick layers

(100 - 300 μm) in order to achieve optimal efficiency due to its weak light absorption for long wavelength light. Consequently they are restricted to a rigid and flat plate designs[1] making them unsuitable for use in automobiles and many buildings integration applications, where curved PVs, or flexible substrates are needed.

The basic structure of a thin film PV devices is a hole-transport layer, a light harvesting layer and an electron-transport layer, all of which are sandwiched between two electrodes. The difference in work function between the electrodes generates a built-in electric field that facilities the extraction of photo-generated charge carriers, and at least one of the electrodes must be transparent to allow light into the device.

Perovskite photovoltaics

Perovskites are a class of inorganic materials with the general structure ABX_3 where A is an organic or an inorganic cation in oxidation state +1 or +2 (e.g.: $CH_3NH_3^+$, Cs^+, Rb^+ etc.) and B is a metal cation of oxidation state of +2 and +4 (Pb^{2+}, Sn^{2+} etc) and X is usually either a halide anion or oxygen anion (Figure 1)[2].

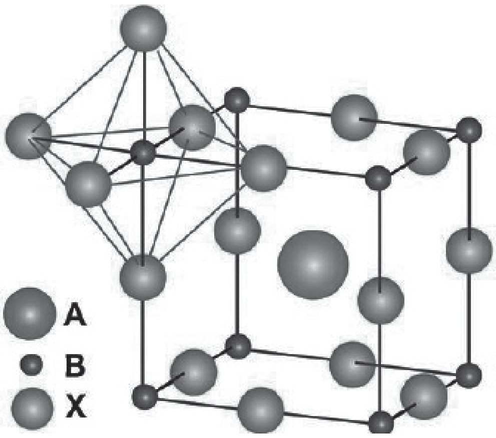

Figure 1: Crystal structure of a perovskite semiconductor with chemical formula ABX_3.

To address the drawbacks of conventional silicon PVs, perovskite photovoltaics (PPV) have begun to emerged.[3] PPV devices using lead (Pb) halide perovskite as the light harvesting semiconductor have shown an unprecedented evolution over the span of less than a decade, with the power conversion efficiency increasing from 3.8% in 2009[4] to 25.2% in 2019[5]. The ease of synthesis of perovskites is a key reason for the rapid and intensive research interest in this area. Lead halide perovskites are also compatible with lightweight flexible substrates[6] because they can be processed from solution at low temperature[7], which ensures a greatly reduced energy outlay in production in comparison to conventional silicon solar cells, and are amenable to facile tuneability of the absorption spectrum via halide mixing/exchange, which is important for applications where the aesthetics are important such as buildings integration applications[8]. Most importantly PPVs offer a potentially very low carbon footprint in production as a result of the low processing temperature and potential for fast roll-to-roll manufacturing, so they can return the energy used in their production within a few months of installation, much less than the 1 year energy payback time of conventional silicon PVs[9].

PPV device architecture and operating principles

The typical structure of a PPV device consists of a light harvesting semiconducting layer sandwiched between electron and hole transporting materials (Figure 2). The charge transporting layers are chosen to ensure optimal alignment of the electrode Fermi levels with the relevant band edges in the light harvesting semiconductor.

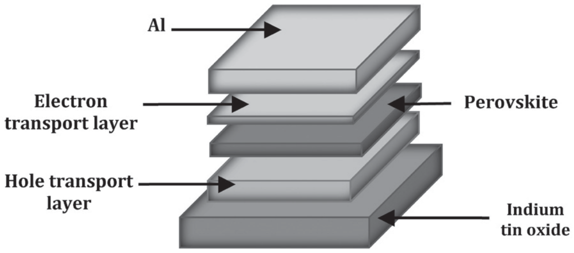

Figure 2: Simplified device architecture of a general perovskite PV device

Initially light passes through the transparent, wide band gap metal oxide electrode; usually Indium tin oxide (ITO). The light harvesting material absorbs photons of light with energy equal to or greater than the band gap via the excitation of electrons from the valence band into the conduction band. Due to the relatively large dielectric constant in perovskite semiconductors the photo-generated electron and hole are not coulombically bound to one another at room temperature. These free charge carries are selectively extracted by an electron transport layer (ETL) and a hole transport layer (HTL) respectively. The separated charge carriers move from their respective transport layers to Fermi level (Ef) of the respective electrodes from which they can flow into the external circuit.

When the two materials in the PPV device come into contact, charge transfer will occur causing an alignment of the Ef, as the electrons will move from higher lying Ef to the material with the lower lying Ef. The equilibration of the Efs of the perovskite and the metal results in formation of a depletion region (W) where all of the transferred charge is concentrated. This charge transfer causes a VL shift at the interface forming a Schottky barrier.[10] (Figure 3).

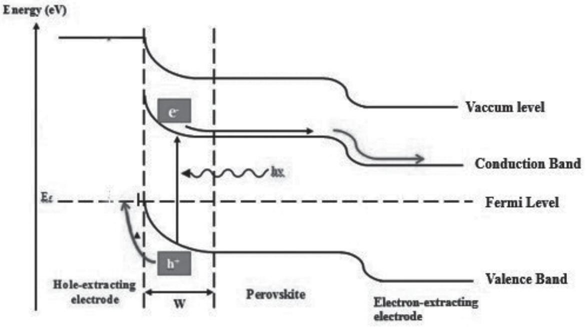

Figure 3: Band diagram for the operation of a Schottky PV device.

The disadvantage of lead halide perovskites for utility in PV devices is the possibility of lead contamination of the environment due to failure of the device encapsulants or improper disposal at the end of life, which is a barrier to commercial exploitation in many parts of the world.[11] This is because lead is well-known to be a highly toxic element that accumulates in the food chain[12] and lead halide perovskites readily decompose upon exposure to moisture and water to form lead compounds with significant solubility in water.[13] Consequently, there is great interest in the development of lead-free alternatives matched to the needs of PV applications.

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Natural Resources in Sri Lanka

Value addition of gemstones of Sri Lanka

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Sri Lanka is one of the five major gem-producing countries in the world (others are; Brazil, South Africa, Thailand and Myanmar). According to Central Bank reports, 2% of the total export revenue of the country comes from gem exports. The gem industry is a high value added industry and the value-addition per carat (weight measuring unit, 1 carat = 200mg) of gemstone is as high as 70% - 90%.

Gems are minerals and have widely varied chemistry. According to mineralogical and physico-chemical properties gemstones are classified into gem varieties. From about two hundred gem varieties that found in world, about seventy are found in Sri Lanka. Following are the major varieties out of them;

- Sapphires (Al_2O_3)
- Spinels ($MgAl_2O_4$)
- Topaz ($Al_2SiO_4(F,OH)_2$)
- Chrysoberyls ($BeAl_2O_4$)
- Beryls ($Be_3Al_2(SiO_3)_8$)
- Tourmalines (a complex borosilicate)
- Garnets ($Ca_3Al_2(SiO_4)_3$)
- Zircons ($ZrSiO_4$)
- Quartz (SiO_2)
- Moonstones (KAl_3SiO_8)

Gems are mined as rough stones. Before entering the market they are subjected to cutting and polishing, at the lapidaries. This is the basic value-addition step of gemstones and it is actually a physical process.

The value of a gemstone depends on four factors, which are known as 4 Cs. They are;

- Colour
- Clarity
- Cut
- Carat weight

Upgrading these properties could add value to gemstones. A cut and polished gemstone has a definite carat weight and cut, but its clarity and colour could be further upgraded by subjecting it to treatment techniques, which are basically physico-chemical reactions. Commonly used treatment techniques are (Nassau, 2001);

- Heat treatment
- Colour diffusion (surface diffusion)
- Bulk diffusion (lattice diffusion, e.g. beryllium treatment)
- Irradiation
- Impregnation
- Laser treatment
- Surface treatments (e.g. plating and chemical vapour deposition)

All of these techniques are secondary value-addition steps. To carryout them successfully, a wide knowledge of science & technology is essential.

The heat treatment of gemstones is well established and popular in Sri Lanka. A few government establishments (e.g. Gem and Jewellery Research and Training.) and many private institutions practice this technique. It is a process where gemstones are heated by a furnace (Plate 1), up to high temperatures but not exceeding the melting points of gemstones (Nassau, 1984).

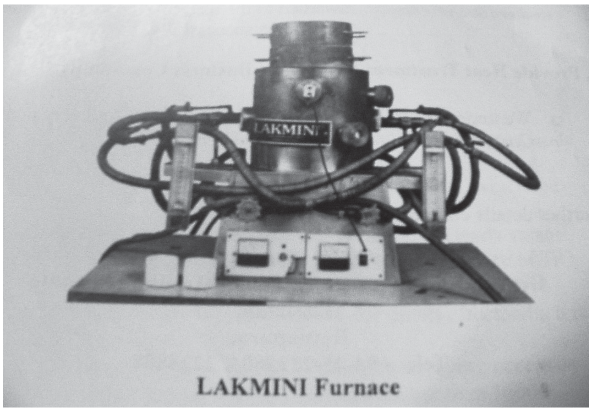

Figure 1: Popular heat treatment furnace (Courtesy of Lanka Refractories Ltd.)

The body colour of a gemstone is a result of;

- transition metal ions and their oxidation numbers,
- colour centres and

- charge transfer transitions

During heat treatment, high temperature chemical reactions (e.g. oxidations and reductions of transition metal ions in gemstones) take place. This will finally results in a change in colour. Many gem varieties (e.g. sapphires, zircon, topaz, quartz etc.) could have added value by heat treatment, but their colour changing temperatures are different from one variety to another.

Heat treatment of “geuda” to yield blue sapphires is popular in Sri Lanka. Geuda is low value sapphire, which is milky or gray in colour. It can be turned into high value blue sapphire by heat treatment. According to market blue sapphires are about 2-3 times more valued than the geuda.

In geuda stones TiO_2(s) (rutile), Fe^{2+} and Fe^{3+} ions present. When geuda stones are heated under reducing conditions (using CO (g) as the reducing agent) at around 1800 ^{0}C (melting point of sapphire is 2050 ^{0}C) the following chemical reactions take place (The Sri Lankan Geuda, 1993);

TiO2(s) dissolves and diffuses into the structure of geuda

$TiO_2(s) \rightarrow Ti^{4+} + 2\,O^{2-}$ reaction 1

$2\,O^{2-} \rightarrow O_2 + 4e$ reaction 2

reaction 1+2, $TiO_2(s) \rightarrow Ti^{4+} + O_2 + 4e$

$Fe^{3+} + e \rightarrow Fe^{2+}$

$Fe^{2+} + Ti^{4+} \rightarrow (Fe, Ti)^{6+}$

$(Fe, Ti)^{6+}$ ion (Ferro titanium complex ion) gives the blue colour of blue sapphire resulted by the heat treatment of geuda.

Research on colour diffusion of topaz was successfully carried out in Sri Lanka. In this method a paste of diffusion material including transition metals pasted on the surface of the colourless topaz stones, and then left to dry. Then these stones are subjected to heat treatment at temperature around 900 0C. Transition metals present in the paste will diffuse into the stone and induce a colour layer on the surface of the stone. By this technique different coloured topaz could be obtained from colourless topaz stones.

Research on gamma irradiation of water-clear quartz was carried out at Atomic Energy Authority of Sri Lanka by the author. In this method quartz is subjected to small dosages of gamma rays produced by a Co60 gamma irradiator. Colourless quartz was turned into smoky colour quartz, which is more valuable than water-clear quartz. When considering the chemistry of this process, quartz is SiO2 and during its formation on earth, Al3+ replaces a minor quantity of Si4+ of the SiO2 lattice.

$$(SiO_4)^{4-} \xrightarrow{Si^{4+} \text{ replaced by } Al^{3+}} (AlO_4)^{5-}$$

Electronic arrangement around $(AlO_4)^{5-}$ is not stable when compared to $(SiO_4)^{4-}$ and an electron could be easily displaced by supplying necessary energy. By gamma irradiation this required energy could be supplied easily.

$$(AlO_4)^{5-} \xrightarrow{\text{an electron displaces}} (AlO_4)^{4-}$$

This makes an electron deficient or a hole on the $(AlO_4)^{4-}$ion. Since this hole could absorb energy from the electromagnetic radiation resulting in colour to the quartz, which is known, as hole colour center. This hole colour center results in a smoky colour to the colourless quartz.

Figure 2: Co 60 Gamma irradiator at Atomic Energy Authority of Sri lanka

To conclude this article it could be said that the heat treatment of geuda is well established in Sri Lanka. Research on colour-diffusion of topaz and gamma irradiation of quartz is also successful and they could be introduced to the market. Applications or research on any other treatment techniques were not reported.

More research into the physico-chemical aspects of value-addition of gemstones is needed. By applying such treatments 100% - 500% value-addition on cut and polished gemstones could be achieved. Therefore such research may contribute to the country's economy through the export of more value added gemstones.

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Guest Articles

CRISPR/Cas system and targeted genome editing

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The discovery and advancement of different genome editing and re-engineering techniques and tools has been a major focus in Molecular Biology over the decades, as the ability to alter the genetic composition of biological systems goes a long way in numerous advantageous applications. Genome editing has been achieved by means of engineered, targeted nucleases as molecular scissors[1,2] where DNA is inserted, deleted or replaced to generate desired modifications with high precision. A number of such genome editing technologies have been exploited in research and applications in recent years such as Zinc-finger nucleases (ZFNs)[1] and transcription activator-like effector nucleases (TALENs), where targeted DNA double strand breaks are generated in specific genome locations, employing an active endonuclease domain associated with a DNA binding protein[2,3]. Even though specific targeting of the genomic loci could be achieved, the need to design, simulate and model target specific DNA binding proteins compensated the efficacy, accuracy and the convenience of the above techniques[4,5].

Clustered regularly interspaced short palindromic repeats (CRISPR) along with CRISPR associated (Cas) nucleases have collectively given rise to another such approach. The emergence of CRISPR- Cas systems as genome engineering and manipulation tools remarkably revolutionized many research arenas as a powerful, versatile and convenient tool[3,4,6–8] with high efficacy[3], contrasting to many prevailing genome editing techniques. CRISPR- Cas systems employ sequence specific, programmable endonucleases to precisely edit and engineer endogenous genomic loci of biological systems[3,6,8,9] to generate desirable, beneficial genetic modifications. These endonucleases are guided by designed RNAs that binds to target DNA by complementary base pairing. This technique has been proven applicable for a wide range of species[2,4–7] to harness in numerous schemes in research arena related to genomic editing and gene therapy. Approaches by *in vitro*, *in vivo* and *ex vivo* means to correct diseases like Cystic fibrosis, Retinitis pigmentosa and Duschenne muscular dystrophy, human hereditary liver diseases and to impose mutations in HIV-1 to reduce transfection in humans are few such examples[6].

CRISPRs and Cas endonuclease proteins comprise the CRISPR/Cas systems which naturally occur in a wide variety of prokaryotic species as an adaptive immune mechanism against viruses and other invasive genetic material[3,5,7,12–14]. Once confronted with an invasion, a short fragment of that exogenous genetic context will be integrated into an array in the CRISPR loci as a new spacer in the bacterial genome. The subsequent transcription of the CRISPR locus of the bacterial genome will eventually generate transcripts called CRISPR RNAs (CrRNAs) from the acquired spacers. CrRNA will guide and assemble an intracellular endonuclease (Cas) to target, cleave and destroy the invading genetic material in a sequence specific manner (Figure 1)[7,12–14]. Hence this is a DNA encoded, RNA guided nuclease system for sequence specific target DNA cleavage[6,8].

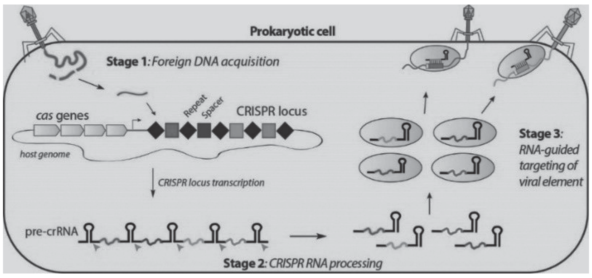

Figure 1: CRISPR mediated immunity in prokaryotes[1].

CRISPR-Cas systems are comprised of three major components and each have mandatory roles in the process of sequence specific target DNA cleavage. CrRNA contains the RNA sequence that is complimentary to the target DNA sequence, which directs to the target DNA and binds to it by complimentary base pairing. The CrRNA guides and assembles a Cas endonuclease to the specific target which generates a double stranded break (DSB) at the target site. There is a need for the presence of a photospacer adjacent motif (PAM) sequence in the target DNA for the generation of the DSB at the target site, as the PAM sequence is needed for the precise and proper assembly of the CrRNA and Cas ribonucleoprotein complex at the target locus[3,6–9,12,14].

CRISPR-Cas systems are divided into two main classes, which are further classified into six types and several sub-types[14]. The classification is based on the type of Cas nuclease employed and the subtle differences in the mechanism of target DNA cleavage. In class 1 CRISPR-Cas systems (types I, III and IV), the effector consists of a multi-protein complex whereas class 2 systems (types II, V and VI) use only one effector protein[3,14]. Furthermore, the PAM sequence could also vary depending on the specific CRISPR system[8,13].

CRISPR-Cas9 (type II) system

Amidst the several types of naturally occurring CRISPR/Cas systems, type II found in *Streptococcus pyogens* is used to engineer CRISPR/Cas9 technology as a genome editing tool and beyond, due to its less complexity[8]. The *S. pyogenes* type II CRISPR locus contains four genes. One gene encodes Cas9 nuclease and another two encode two noncoding CRISPR RNA components; trans-activating CrRNA (tracrRNA) and the precursor crRNA (pre-crRNA).

Pre-crRNA is an array comprised of transcripts of the spacers interspaced by identical direct repeats[3,7,] which produce single guide RNA (sgRNA) s upon processing. The tracrRNA is the auxiliary component of the CrRNA that facilitates processing of the crRNA array into discrete units and aids in the assembly of the ribonucleoprotein complex by maintaining the correct conformation of the Cas nuclease[9]. In addition, the CrRNA has a guide sequence of 20 nucleotides specific to the target, which binds to the target by complimentary base pairing and guides the cas9 to the specific 20 bp target DNA[7,8,15,16] (Figure 2). In type II systems, the preferred PAM sequence is found to be NGG[7,8,16,] present upstream towards 5' end of the target and on the complimentary strand of the target.

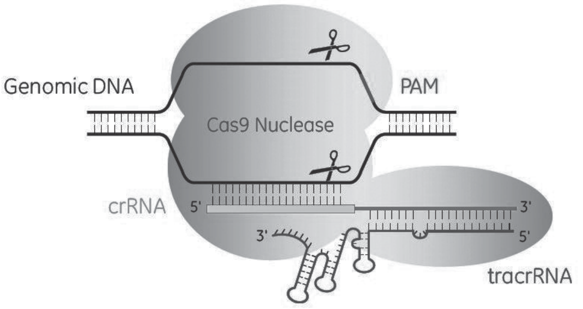

Figure 2: The mechanism of DSB generation in CRISPR-Cas9 systems.

The Cas9 nuclease embody two active catalytic domains with endonuclease activity; namely RuvC and HNH. Upon correct assembly of the CrRNA and Cas9 ribonucleoprotein complex on the target locus, these two domains come into play to produce cleavages in the target, giving rise to a DSB[7,9,12,16] (Figure 2).

The DSBs generated by Cas9, are repaired in one of two ways, promoting gene editing. The endogenous repair machinery of the cell employs the error-prone non-homologous end joining method (NHEJ), which executes by incorporating random nucleotides into the DSB, thereby producing random indel mutations (Figure 3) at a high frequency. NHEJ borne indel mutations occurring within a coding region of a gene can lead to gene knockout due to frameshift mutations and generation of premature stop codons[3,7,8,15,17,18]. Alternatively, an exogenous template DNA with homologous arms to the flanking region of the DSB can be introduced to induce the homology directed repair (HDR) pathway (Figure 3) which results in more precise and specific editing[3,7,8,18]. This short template DNA sequence can harbour any sort of insertion or alteration, allowing the integration of any desirable DNA sequence at the target site. Cells that are dividing may use either the NHEJ or HDR pathways whereas cells that are non-dividing may only use the NHEJ pathway[5,8].

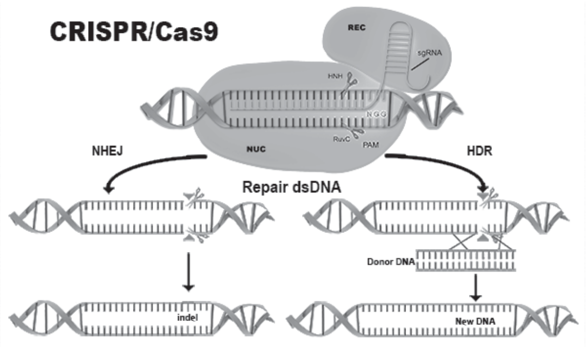

Figure 3: DSB generation by CRISPR-Cas9 and repair pathways.

Therefore, this overall model containing the CrRNA, Cas9 endonuclease and the PAM sequence, can be adapted to other desired cellular systems and specific targeted modification can be achieved by designing the specific crRNA bearing the complimentary sequence corresponding to the target DNA loci.

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Chemistry of Perfumes

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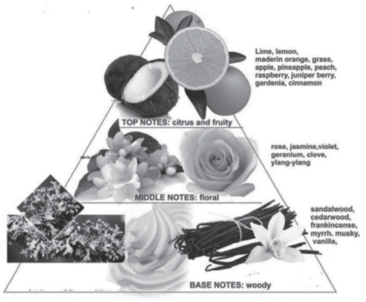
Perfumes or fragrances are the fusion of science and art: where chemists become creators and molecules make memories. Fragrances are unique. They are designed with care, passion and ingenuity. They give pleasure to billions of people around the world, who use and enjoy fragrances every day - from a fresh-smelling shampoo to freshly-laundered clothing. The word *perfume* derives from the Latin "*per-fumum*" meaning *through smoke*. The art of making perfumes "*perfumery*" has begun for more than 4,000 years - from ancient Egyptians, through the Persians, Greeks and Roman Empires and up to the modern day. Scents or the fragrances inspire a range of positive emotions, such as joy, pleasure, cleanliness, attraction, expression of status and for spiritual faiths.

The first perfume was the fragrant flower and continued to be in the present day. The modern perfume was made in 1370 at the command of Queen Elizabeth of Hungary and was known as "*Hungary Water*". Since then many perfumery arts have been developed. Fragrances are chemical compounds with a pleasant, sweet smell. By the 18th century, aromatic plants were being grown in the Grasse region of France to provide the growing perfume industry with raw materials. At present, the fragrance industry in France and England is most extensive and rule the markets in the world. Especially Paris remains the centre of the European perfume design and trade by furnishing the best raw materials, the finest essential oils. Givaudan, Firmenich, Symrise and IFF: International Flavours and Fragrances are the world largest and top ranked companies in the flavour and fragrance industry. The world-famous perfumes; *Angel by Thierry Mugler* from Firmenich, *One Million by Paco Rabanne* from Givaudan and *La Vie est Belle by Lancome* from IFF are few examples for their leading products in the international market.

The essential oils used in perfumes are classified according to their volatility, or the rate of diffusion into the air; hence, each essential oil is expected to have three *notes*. The *note* is an ingredient with one characteristic smell.



Top notes come out first (very volatile): first noticeable smell from a perfume last for few minutes to 30 minutes or less. They are often tangy or citrus-like smells that are easy to smell (*e.g.*: bergamot, juniper berry, cedar wood, lavender, geranium, gardenia, cinnamon, pepper, thyme).

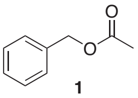
Middle notes often aromatic flowers: they may last for about an hour (*e.g.*: clove, ylang-ylang, lavender, jasmine, rose, pineapple, raspberry and geranium).

Base notes often woody fragrances, last longest or least volatile: they provide an enduring fragrance for longer time (*e.g.*: frankincense, myrrh, sandalwood, chocolate and vanilla).

Combination of two or more *notes* creates a new smell, which is different from each *note*. There are more than thousands of raw materials could be used as notes. Therefore, there is a possibility of generating infinite number of smells! For example, ***Fougère*** is one of the main families in perfumes. They are made of mixtures of *notes*: scents of lavender flowers, oakmoss (from lichens), bergamot (from citrus), coumarin (scent of newly-mown hay).

Most substances used in perfumery industry are derived from plants, animals, microorganisms, and by chemical synthesis. As in the natural sources contain many ingredients, it is a generally complex mixture. The use of synthetic chemicals started from 19th century with the development of organic chemistry. Synthetic molecules are less expensive to prepare, rather than isolating alternatives from the natural substances. Most natural substances may degrade at different acidic, basic, neutral and oxidizing media by changing their odour and colour. Many naturally occurring compounds are also not stable in bleach, laundry powders and soaps. Therefore, synthetic chemists developed synthetic molecules that can withstand for these natural products. As a result, by now, a wider range of consumer products contain durable perfumes.

The pleasant and finest odour of roses or jasmines is particularly from their flowers. But all the flowers of the plants do not contain the active ingredient. Yet it is not the blossoms alone; in some plants the fragrant substances are present in every part (pines and mints), only in the fruits (nutmeg, vanilla), only the rinds of the fruits (lemon, oranges), and some plants are entirely odourless but their roots stock the fragrant substances. It is found that benzyl acetate (34%, **1**), benzyl benzoate (24%, **2**), linalool (8%, **3**), benzyl alcohol (5%, **4**) and *cis*-jasmone (3.5%, **5**) account for the *base note* fragrance of jasmine. The major ester compounds, benzyl acetate and benzyl benzoate could be synthesised easily by esterification reactions. Due to its commercial viability, jasmine flavoured incense sticks, perfumes, deodorants, toilet soaps and other cosmetic products are commonly available.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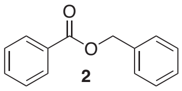
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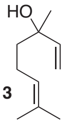
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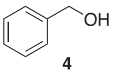
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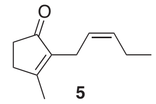
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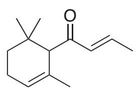
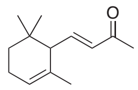
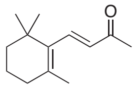
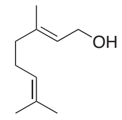
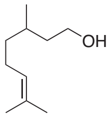
Similarly, violet flower oil was the most expensive of all essential oils and it is still economic to produce. To produce one kilogram of violet oil; 33,000 kg of violet blossoms are needed. As an alternate some industries use violet leaf as a substitute, but the smell is not quite same as that of the flower. In 1893, ionoes were synthesised which revolutionized perfume industry. Today almost all perfumes include them as they blend well with other perfumery materials. The damascones are a group of ionones and they are components of rose oils and have very intense fruity-floral smell. Rose notes are now available as inexpensive synthetics such as geraniol, citronellol, and 2-phenylethanol.

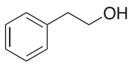

Damascone


α-Ionone

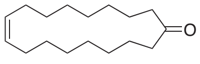

β-Ionone


Geraniol

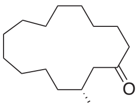

Citronellol


2-Phenylethanol

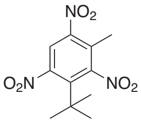
Musk is a glandular secretion from animals especially from male Musk deer which is extensively used in perfumery in 19th century. Till today natural musk is one of the most expensive animal products in the world. Not only the musk deer, there are other animals that priced for perfumery industry; such as, Civets (cat like animal with a long tail, yellow paste like faecal is used in perfumery industry). Macrocyclic muscone and civetones are the main fragrant compounds of musk and civets. During 1888, while searching for explosives, Albert Baur discovered pleasant musky smell in the product "musk Baur" formed with trinitrotoluene with *tert*-butyl halides. Later he developed musk ketone which was a major perfumery ingredient. Subsequently many derivatives were prepared using musk synthetics, and famous musk perfumes are now available in the market (*e.g.* Celestolide by IFF and Versalide by Givaudan).



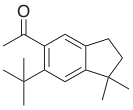
Civetone



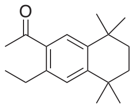
Muscone



musk Baur

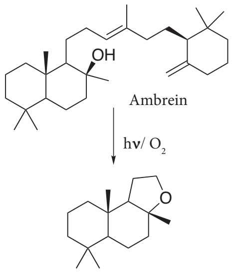


Celestolide
IFF



Versalide
Givaudan

Ambergris (a waxy substance found in the intestines in sperm whales and expel as a faecal matter) is one of the rarest and high valued perfumery ingredients. The formation of Ambergris is due to the reaction of sunlight, waves and oxygen in air. It favours the conversion of odourless Ambrein to Ambrox (Ambergris).

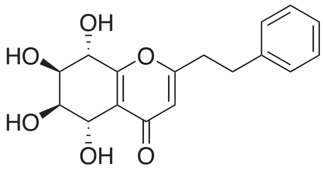


Ambrox (ambergris)

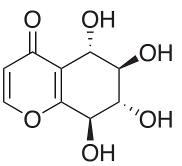
Other examples include Castoreum, the fluid from castor sacs of American beaver; and Hyraceum, rocklike excreta of Rock hyrax which releases a dark oil with intense and complex scent.

Agarwood is a resinous product produced in the heartwood of *Aquilaria, Gyrinops, Aetoxylon* and *Gonystylus* species. Once the heartwood of these species is infected with the fungi or bacteria as a defence mechanism, the dark, highly fragrant and economically valued oleoresins are produced. Agarwood resin is also found in Walla Patta tree, thus, illicit cutting and smuggling of these trees is being reported in Sri Lanka.

Agarotetrol and isoagarotetrol are the common chromones which are the important contributors to the sweet, fruity and long-lasting scent of agarwood. These two natural compounds are considered as potential marker compounds to grade the agarwood products.



Agarotetrol



Isoagarotetrol

The common techniques used for identification and characterisation of active components of fragrances are GC and LC-MS, which helped the synthesis of these valuable organic molecules. As a result, search for new *notes* and thereby *accords* become easier. Similarly, now many synthetics are available, which mimics the natural behaviour of fragrant substances. Therefore, synthetic chemistry brings more creativity to perfume industry and provides affordable and safer ingredients to discover unique eternal fragrances.

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Student Corner

Student Corner

Isomerism in Coordination Compounds

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Isomers (compounds with the same chemical formula) can be broadly classified into (i) **stereoisomers** (*e.g.* geometrical and optical) with the same connectivity but having different spatial arrangements and (ii) **structural isomers** with different connections between atoms. We are quite familiar with the geometrical (*cis* and *trans*) and optical isomers (*e.g.* enantiomers) of organic molecules where the valency of carbon is **four**. Coordination compounds can form several different types of isomers because metal centres, often, can have coordination numbers higher than four and can adopt different geometries. The following are the common structural isomers of coordination compounds: **ionization**, **hydrate**, **linkage** and **coordination**.

Ionization isomers

Ionization isomers have the same **empirical formula** but differ in the **coordinated anion(s)** thus, yielding different ions **when dissolved in a solution**. Furthermore, ionization isomerism is shown by salts, often involves the exchange of an **anionic ligand** (*e.g.* halide, sulphate, *etc*) between the complex ion (**coordination-sphere**) and the remainder of the salt (**ionization-sphere).** For example, $[CoBr(NH_3)_5]SO_4$ and $[Co(SO_4)(NH_3)_5]Br$ are such isomers. They have the same **chemical composition**, $CoBrSO_4(NH_3)_5$, but differ in ions present in an aqueous solution. In water, $[CoBr(NH_3)_5]SO_4$ produces sulphate ions whilst $[Co(SO_4)(NH_3)_5]Br$ gives bromide ions.

Hydrate isomers

This is analogous to ionization isomerism except that **water** molecule(s) (a **neutral ligand**) replaces the **ionic ligand**, bromide. For example, there are **four** different **octahedral** Cr(III) compounds with the **composition** $CrBr_3{\bullet}6H_2O$. They are given below.

Compound	No. of Br^- ions
$[Cr(H_2O)_6]Br_3$	3
$[CrBr(H_2O)_5]Br_2.H_2O$	2
$[CrBr_2(H_2O)_4]Br.2H_2O$	1
$[CrBr_3(H_2O)_3].3H_2O$	0

Linkage isomers

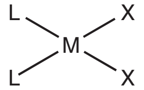
Some ligands can bind in **more than one way** hence they are called **ambidentate** ligands (*e.g.* NCS and SCN; thiocyanate and isothiocyanate). Complexation of these ligands can result in isomeric compounds, known as **linkage isomers**, with different modes of bonding to the metal centre. For example, the coordination compound with the empirical formula $MnNCS(CO)_5$ shows two linkage isomers $[MnNCS(CO)_5]$ with a Mn-N bond and $[MnSCN(CO)_5]$ with a Mn-S bond. The NO_2 ligand is also an ambidentate ligand and can use either N or O as the donor atom.

Coordination isomers

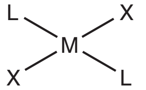
When both the **cation** and the **anion** are of complex ions of two different metal centres (*e.g.* Co and Cr), the distribution of ligands can vary between the two metal centres giving rise to isomers. This isomerism can be considered as an extreme case of ionization isomerism. *e.g.* $[Co(NH_3)_6][CrBr_6]$, $[Cr(NH_3)_6][CoBr_6]$ are **coordination isomers** with the same empirical formula, $CoCrBr_6(NH_3)_6$.

Geometric isomers

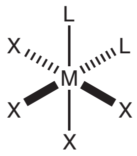
Geometric isomers (or *cis*- and *trans*- isomers) occur when the relative positions of ligands in a **disubstituted** compound are different. This is commonly found in square-planar complexes of type $[MX_2L_2]$ and $[MXYL_2]$; and octahedral complexes of the type $[MX_4L_2]$.



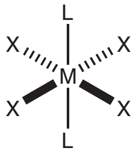
cis-isomer



trans-isomer

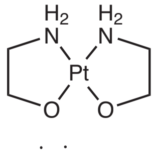


cis-isomer

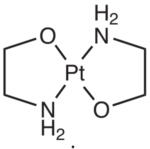


trans-isomer

Geometric isomerism can also occur in square-planar *bis*-chelate complexes if the chelating group is **not symmetrical**. For example, $[Pt(NH_2CH_2CH_2O)_2]$ can have two *cis-trans* isomers.

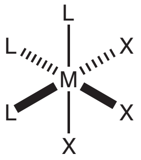


cis-isomer

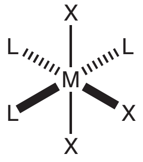


trans-isomer

Trisubstituted octahedral complexes of the type $[MX_3L_3]$ can exist in two forms; (i) *facial* isomer or *fac*-isomer and (ii) *meridional* isomer or *mer*-isomer. Note that $[MX_3L_3]$ does not show *cis-trans* isomerism.



fac-isomer

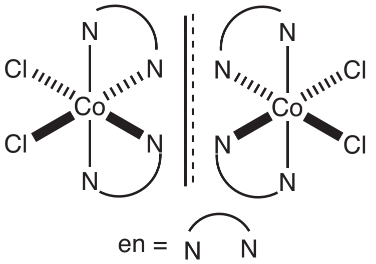


mer-isomer

Optical isomers

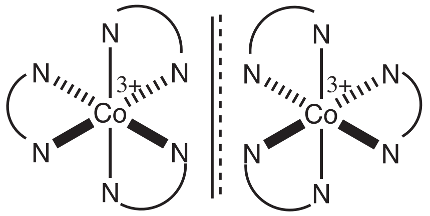
Optical isomers exist when the mirror image of one isomer is **not superimposable** on the other. Such a pair of isomers is called **enantiomers**. The isomers are prefixed either *dextro* or *laevo* (often abbreviated to *d* or *l*) depending on the direction they rotate the plane of polarized light. **These compounds do not possess either a plane of symmetry or a centre of symmetry**. Optical isomerism is found mainly in octahedral complexes with chelating bidentate ligands, and to a lesser extent in tetrahedral and square-planar compounds.

The octahedral complex *cis*-$[CoCl_2(en)_2]$ has two optical isomers, where en = ethylenediamine = $H_2NCH_2CH_2NH_2$.

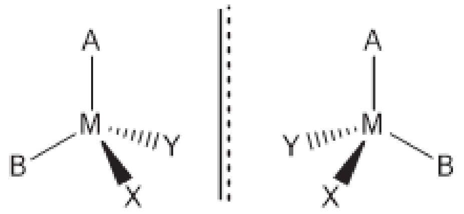


trans-$[CoCl_2(en)_2]$ is **optically inactive** because it has a plane of symmetry.

The cation $[Co(en)_3]^{3+}$ exists in two isomeric forms, which are **non-superimposable** mirror images. Therefore, they are enantiomers.



Optical isomers in tetrahedral complexes are more common. If the complex is of the type [MXYAB], where X, Y, A and B are different ligands, the compound is capable of existing in two optically active forms.



Generally, square-planar complexes of the type [MXYAB] **do not exhibit** optical isomerism because the **plane of the molecule acts as a plane of symmetry**.

Optical isomerism is also possible when the tetrahedral complex contains two **asymmetrical bidentate** ligands. Complexes containing hexadentate ligands can show optical isomerism, *e.g.* the Co(III) complex $[Co(EDTA)]^-$ forms two optical isomers.

Problems

1. How can you distinguish $[CoBr(NH_3)_5]SO_4$ from $[Co(SO_4)(NH_3)_5]Br$?
2. **Draw** and **identify** the three **geometrical** isomers

of $[FeBr_2(CO)(NH_3)_3]$ (**A**). Does (**A**) show optical isomerism?

3. Draw the **geometrical** and **optical** isomers of $[NiBrCl(CO)(NH_3)]$.

4. $[FeBr_2(acac)(NH_3)_2]$ shows **two** geometrical isomers (**B**) and (**C**). (**C**) shows optical isomerism. Draw and identify the structures of (**B**) and (**C**). Draw the optical isomer of (**C**). ($acac^-$ = acetylacetonate ion)

Student Corner

Valence Bond Theory

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Metal centres of *d*-block form coordination compounds with ligands which can donate a pair of electrons. These ligands are known as *sigma* donors or Lewis bases. Some ligands that consist of suitable vacant orbitals accepts electron density from the metal (back donation/bonding) to reduce the high charge density at the metal centre. These ligands (π-acceptors) make more stable complexes with the metal centre. Valence Bond Theory (VBT) is one of the theories put forward by Linus Pauling in 1940 to explain the nature of metal-ligand bonding in metal complexes. The assumptions of VBT are (i) central metal ion make use of vacant *s*, *p* and *d* orbitals and number of empty orbitals used is equal to its coordination number (C.N.), (ii) these orbitals hybridize together to form the same number of degenerate hybrid orbitals, (iii) each ligand has at least one orbital containing a pair of electrons which is donated to the metal centre.

In octahedral complexes, more stable inner-orbital complexes show d^2sp^3 hybridization whilst less stable outer-orbital complexes show sp^3d^2 hybridization. For example, $[CoL_6]^{3+}$ is an inner-orbital complex with a strong field ligand "L" and $[CoL'_6]^{3+}$ is an outer-orbital complex with a weak field ligand "L′" (see Figure 1). The energy of these outer-orbitals is quite high, as a result the outer-orbital complex is reactive (or labile).

Due to the influence of the strong field ligand L, $[CoL_6]^{3+}$ is a diamagnetic low-spin cation with no unpaired electrons, but $[CoL'_6]^{3+}$ is a paramagnetic high-spin cation with four unpaired electrons.

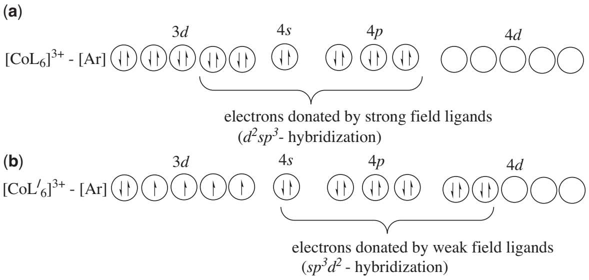

Figure 1: Hybridization of octahedral Co(III) complexes with (a) strong field ligands "L" (b) weak field ligand "L′".

When the C.N. of a complex is four it can have square-planar or tetrahedral geometry. Square-planar complexes have the d^8 electron configuration and are diamagnetic. On the other hand, most tetrahedral complexes are paramagnetic. Thus, square-planar complexes are low-spin complexes having dsp^2 hybridization. Most tetrahedral complexes are high-spin complexes with sp^3 hybridization.

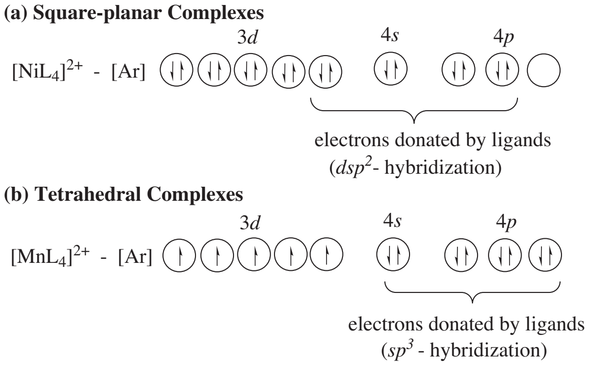

Figure 2: Hybridization of (a) square-planar complexes (b) tetrahedral complexes

Hybridization of *3d*-metal centres vary with the C.N. and the geometry of the coordination compounds as given in Table 1.

Table 1: Hybridizations occurring in the *3d*- metal centres

C.N.	**Hybridization** (orbitals used)	**Geometry**
2	***sp*** ($4s$, $4p$)	Linear
3	***sp***^{2} ($4s$, $4p^2$)	Trigonal-planar
4	***sp***^{3} ($4s$, $4p^3$)	Tetrahedral
	dsp^2 ($3d_{x^2-y^2}$, $4s$, $4p_x$, $4p_y$)	Square- planar
5	***dsp***^{3} (d_{z^2}, $4s$, $4p^3$)	Trigonal-bipyramidal
	sp^3***d*** ($4s$, $4p^3$, $4d_{x^2-y^2}$)	Square-pyramidal
6	***d***^{2}***sp***^{3} ($3d_{x^2-y^2}$, $3d_{z^2}$, $4s$, $4p^3$)	Octahedral (inner-orbital)
	sp^3***d***^{2} ($4s$, $4p^3$, $4d_{x^2-y^2}$, $4d_{z^2}$)	Octahedral (outer-orbital)

Pauling made use of magnetic measurements to find out the number of unpaired electrons in a complex, which helped him to suggest the orbitals involved in the hybridization process.

The limitations of VBT are: it fails to explain the origin of color and magnetic properties of transition metal complexes. Thus, Crystal Field Theory (CFT) has become more powerful theory as it explains those two properties.

Problems

1. Using VBT, predict the hybridization of iron in $[Fe(H_2O)_6]^{2+}$ with $\mu_s = 4.9$ BM.
2. Using VBT, predict the hybridization of Mn in $[MnBr_4]^{2-}$.
3. Using VBT, predict the hybridization of cobalt in $[Co(NH_3)_6]Cl_3$ if the magnetic moment is zero BM.
4. Show that all octahedral complexes of Ni^{2+} are outer-orbital complexes.
5. Using VBT, predict the orbitals involved in the hybridization of the following.

   (a) $[FeF_6]^{3-}$ (b) $[Mn(CN)_6]^{3-}$ (c) $[Fe(CO)_5]$

Student Corner

Opium Alkaloids

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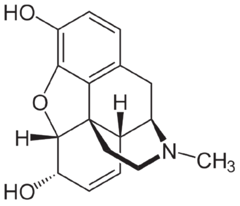
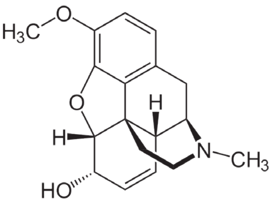
Alkaloids constitute a class of nitrogen containing organic compounds that possess significant pharmacological properties. They occur mainly in plants and to a lesser extent in microorganisms and animals. The name alkaloid or 'alkali-like' was first introduced by the German chemist Wilhemm Meissner in the early nineteenth century.

Opium poppy seed pod

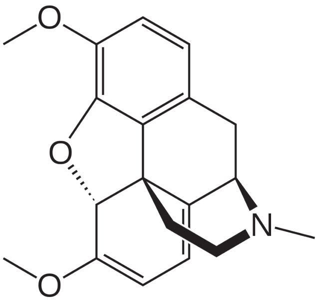
The study of alkaloids began in nineteenth century and the first alkaloid isolated in pure form was morphium by Friedrich Sertuner in 1805. This compound is commonly known as morphine and it is found in opium poppies. Opium is the dried milky exudate obtained from the unripe seed capsules of the opium poppy, Papaver somniferum. Opium has traditionally been smoked for pleasure, but it can also be used as an analgesic, sleep inducer and for treatment of coughs. However habitual users develop a craving for the drug as an addiction.



Morphine

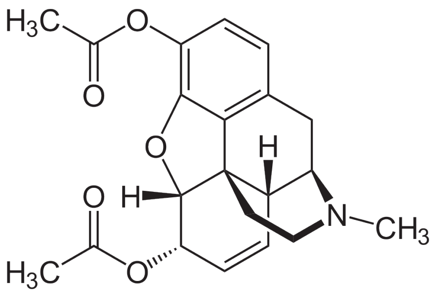


Codein



Thebaine

The principal opium alkaloids are morphine, codeine and thebaine. Morphine is a powerful analgesic and narcotic. Monoacetate ester of morphine is known as codeine and it produces morphine like analgesic effects. Thebaine differs structurally from morphine and codeine due to the presence of a conjugated diene ring system and it is used as a substrate in the semi-synthesis of other drugs. Diacetate of morphine is known as heroin and it is a highly addictive analgesic than morphine.



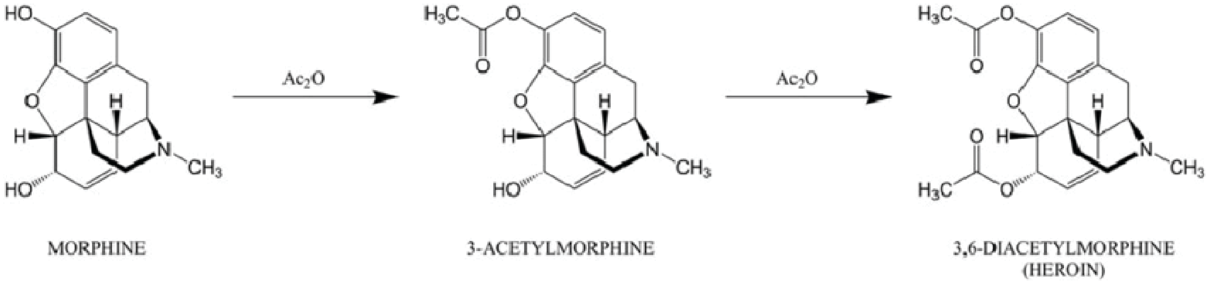
heroin

Is it possible to chemically synthesize heroin from morphine?

Yes. Heroin can be synthesized by treating morphine with acetyl chloride or acetyl anhydride. This is a simple reaction and yields are generally quantitative.

References:

1. Alkaloids: chemical and Biological Perspectives, S.W. Pelletier
2. Drugs of Natural Origin, Gunner Samuelson



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