

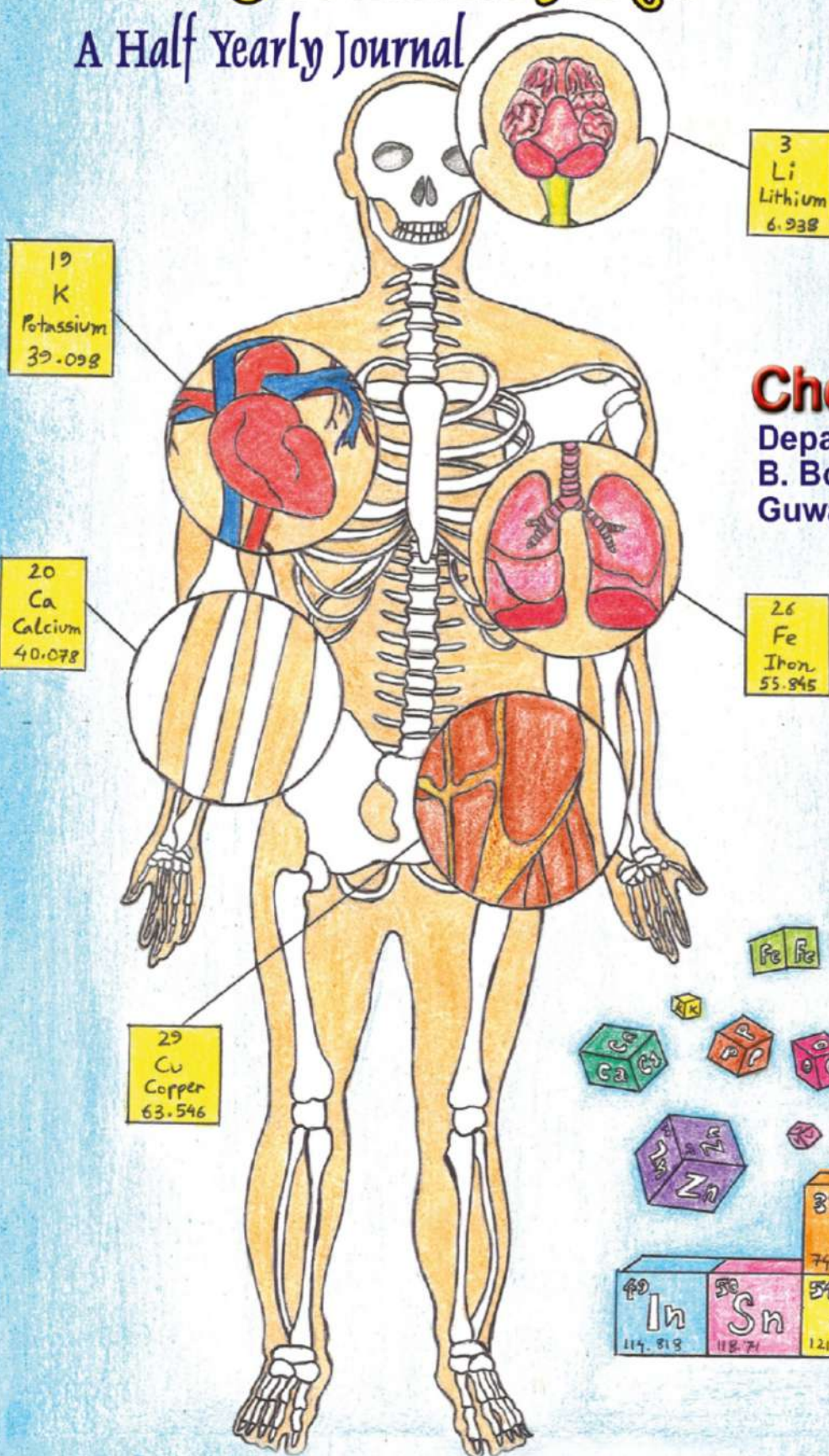
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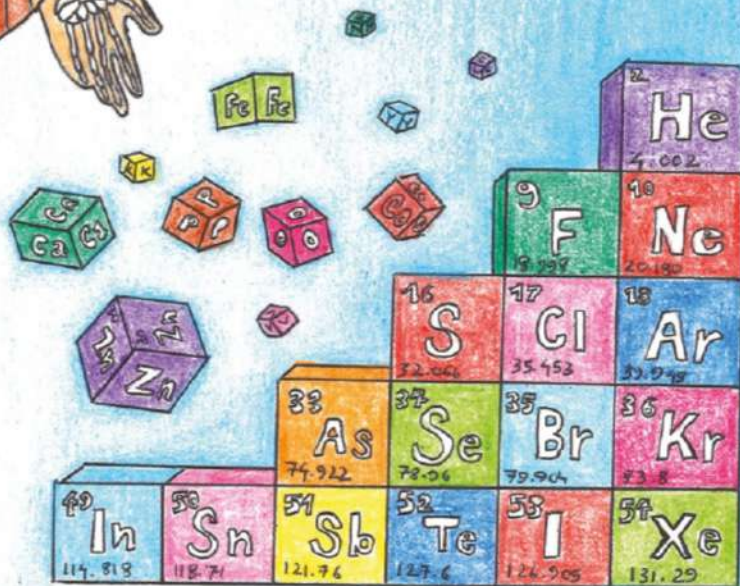
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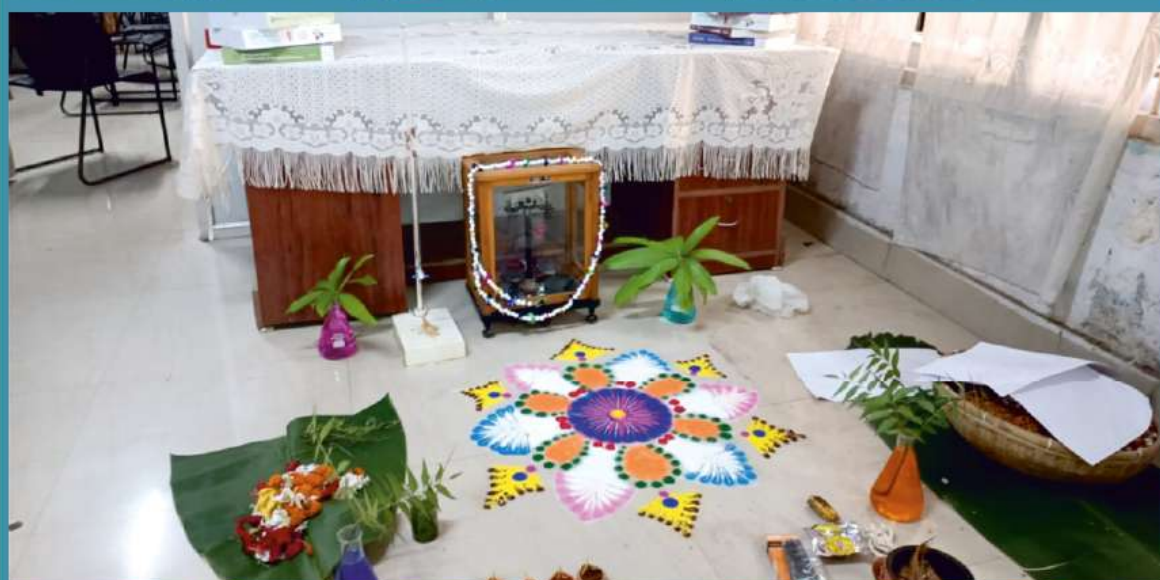
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"Chemistry is necessarily an experimental science: its conclusions are drawn from data, and its principles supported by evidence from facts."

- Michael Faraday

The world around us has shaped up in a dramatic way in these past few hundred years. From simple alchemy to creating bio-engineered cells, we have indeed come a long way. Be it serendipity or someone's genius, technological advances have never ceased and nor will it ever be. But because our eyes are always set on the horizon and not on the surroundings, knowingly or unknowingly we have incurred upon us nature's wrath and we must find a way to leave the world a better place than we found it. As the world currently braces for an energy shortage, there has been an increasing need for alternative, more sustainable energy sources. Replacement of traditional energy shortage units is also underway. Nano-technology has opened up new dimensions to technological improvements.

With the onset of the new year, we are back with another issue of The Chemical Axis and in this issue, we have tried to garner articles based on the recent happenings in the world of chemistry. Articles on Graphene, Silk Protein 'Sericin', Conductive hydrogels, a study on Electrocatalytic Hydrogen Evolution reaction and an article on the perspective of studying abroad is included among numerous other exciting topics. The Students' section includes articles on nano-sensors, nanozymes, sodium-ion battery and an experimental work on

electrophilicity of carbonyl compounds. The series on Bhatnagar Awardees, this time features Dr. Pallikaranai Thirumalai Narasimhan. The series on History of Chemistry is continued in this issue.

Date: 26-01-2023

Place: Guwahati

*The abstract sketched on the cover page has been designed by
Raqtav Neel Kalita on the quotation*

*"The body tends to treat elements in the same column of the
periodic table as equivalents."*

- Sam Kean



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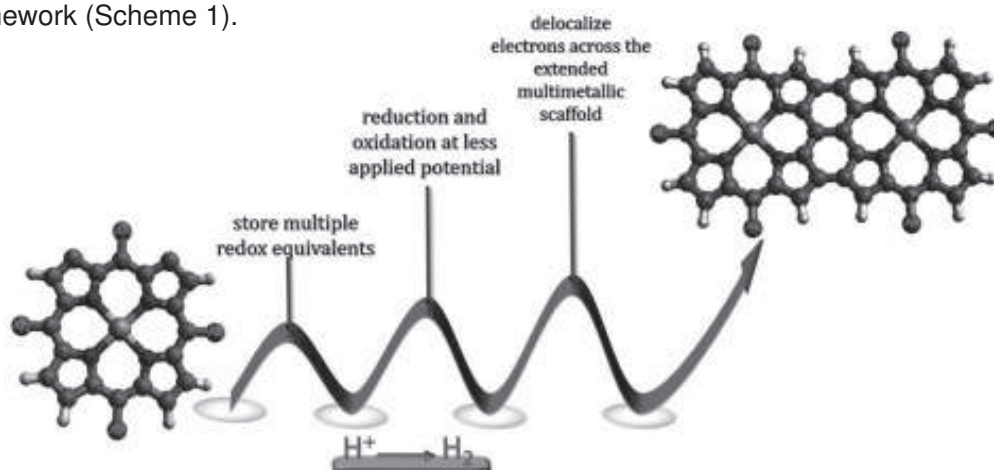
Influence of Extended Conjugation and Functional Groups Towards Metalloporphyrin Catalyzed Electrochemical Hydrogen Evolution Reaction

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Electrocatalytic hydrogen evolution reaction (HER), a sustainable way to produce hydrogen has attracted considerable attention as a new paradigm for energy storage, supply, and transport ¹. To date, elemental platinum is considered as one of the most efficient catalysts for HER; however, its low natural abundance and high cost limit to some extent its large-scale application, prompting researchers to seek alternative nonnoble metal-based catalysts.² Consequently, substantial effort and time has been devoted to finding cheap, efficient and robust catalysts comprising of earth-abundant elements.³ Metal complexes of the porphyrin macrocycle in this context has been explored extensively as catalysts for HER due to high catalytic activity, appreciable stability, and ease of tuning the ligand backbone.⁴ Although, metalloporphyrin monomers have been widely used for energy related small molecule activation, surprisingly, dinuclear analogues of metalloporphyrin, i.e. fused porphyrins remained largely unexplored for the electrocatalytic hydrogen evolution reaction until a recent report by Moore and coworkers highlighting enhanced catalytic activity of the doubly fused dinuclear Cu(II)- porphyrin towards HER compared to the respective monomeric analogue ⁵.

Fused porphyrins are unique structural motifs in which two monoporphyrin units are linked together via β - β , meso-meso, β '- β ' triple covalent linkages.⁶ Metal complexes of fused porphyrins could be considered as promising candidates for electrochemical HER attributed to their ability to undergo reductions or oxidations at lower applied potentials compared to their monomeric counterparts and extensive delocalization of π -electrons across the framework (Scheme 1).

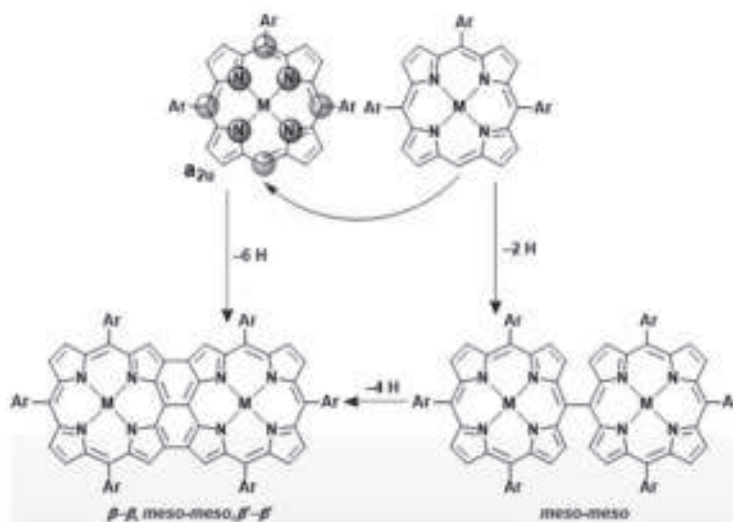


Scheme 1. Advantages of fused porphyrin for electrocatalytic studies

In this context, a bimetallic triply-fused Cu(II)-porphyrin (Cu-1) was synthesized and investigated for its catalytic activity for electrochemical HER. To underline the advantage of the bimetallic catalysts over the monometallic complex (Cu-2), the electrocatalytic activity of both complexes was investigated under an identical experimental conditions.

Results and discussion:

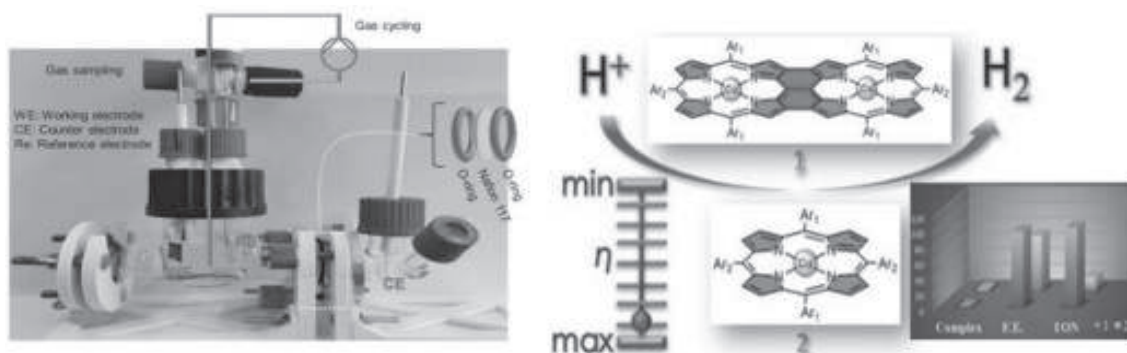
Oxidative C-C coupling reactions facilitated by the dehydrogenation of metalloporphyrins in the presence of organic oxidants result in the formation of triply linked porphyrin oligomers. The most widely accepted mechanistic pathway of oxidative C-C coupling reactions involves a nucleophilic attack of the neutral porphyrin on the porphyrin radical cation (SOMO). Since the meso-position is considered as most electron rich nucleophilic sites



Scheme 2. Oxidative C-C ring closure pathway

in most case, the orbital coefficients of the singly-occupied molecular orbital of the porphyrin radical cation govern the regioselectivity of the coupling reaction. In the case of electro-inactive metals such as Zn, an unpaired electron in the porphyrin radical cations is located in the π -orbital of a_{2u} symmetry justifying the formation of triply fused porphyrin dimers (Scheme 2).

Besides various spectroscopic methods in combination with magnetic measurements to obtain details about the molecular structures of the complexes, electrochemical methods were mainly employed to elucidate the catalytic efficiency. The advantages of extended electron delocalization across the fused scaffold facilitated dramatic reduction of the energy differences between the frontier molecular orbitals in the case of Cu-1 compared to Cu-2, which was clearly indicated by the anodic shift of the reduction potentials. This indeed formed the basis for further investigation in the presence of a proton source (trifluoroacetic acid, TFA), by titrating the increasing concentration of a 0.01 mM solution of TFA onto the electrolyte solution of the complexes. Comparison of the catalytic activity of Cu-1 and Cu-2 furnished a significant reduction of the overpotential (480 and 800 mV for Cu-1 and Cu-2, respectively) by ~ 320 mV. While, controlled potential electrolysis at -1.05 V resulted in significantly higher turnover number and faradaic efficiency of Cu-1 compared to Cu-2 (Scheme 3). On the other hand, tuning of the peripheral functional groups in two different Ni-containing triply fused metalloporphyrins (Ni-1 and Ni-2) revealed that Ni-2 with large alkoxy groups at the peripheral position catalyses proton reduction at lower overpotential and higher activity in comparison to analogous Ni-1 with moderate functional groups, as confirmed by the higher i_{cat}/i_p and turnover frequency values. Mechanistic elucidation of the reaction pathway using the doubly reduced species revealed heterolytic protonolysis leading to the generation of H_2 .



Scheme 3. The diagram on the upper left depicts the setup for controlled potential electrolysis. While the diagram on the upper right illustrates various catalytic parameters utilized for the comparison of the activity in Electrochemical HER

In summary, the bimetallic copper complex (**Cu-1**) of a triply-fused porphyrin framework was synthesized to generate a highly efficient molecular catalyst for electrocatalytic proton reduction. Considering the excellent catalytic parameters obtained from the investigation (low overpotential, stability of the molecular catalyst, high turnover frequency and numbers, unprecedented current densities and high rate constants), we expect that metal complexes with triply fused biporphyrin ligands will play a very important role in energy related electrocatalytic work in the future.

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■ ■ ■

"Chemistry begins in the stars. The stars are the source of chemical elements, which are the building blocks of matter and the core of our subject"

- Peter Atkins

Conductive Hydrogels: Merging Humans and Machines

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The human body is regarded as the most efficacious machine in the world since its inception. The smartness, efficiency, as well as stability in any environmental conditions, is much prominent that to date no other machines can replicate the intelligence of a human body despite all the technological advancements. Keeping eye on the mechanical properties of traditional machines, which are made of hard, dry, abiotic materials, sustainably differs from the soft biological tissues. To bridge the gap between the structural dissimilarities of the human body and machines, hydrogels have emerged as a promising material that replicates the properties of any smart materials as well as the physical and mechanical properties of biological tissues. Owing to its unique flexibility and hydrated matrix, the hydrogels act as a potential candidate to mimic smart tissue-like soft material.^{1,2}

In recent years, intensive efforts have transformed conventional materials into soft, flexible, tissue-like structures without altering the intrinsic properties of the material. To fabricate these kinds of soft materials the correlation between the hydrogels and biological tissues needs to be understood. (Table 1)

High water content	The human body contains almost 70% water of the body weight which serves critical biological, chemical and physical processes. But, most engineering materials such as silicon, metals, and plastics are dry, whereas, hydrogels resembling tissues have high water content (~90% of weight), and can closely mimic and minimize the potential issues caused by dry foreign materials.
Mechanical softness	The human body is largely composed of soft tissues except for teeth and bone, where Young's moduli lie in the range of 1Pa to 1MPa, whereas most conventional solids that are used in biological applications exhibit Young's moduli in higher magnitudes. By contrast, hydrogels can have Young's moduli almost similar to soft tissues and also can be tuned, owing to their highly hydrated fibril network compositions.

Biocompatibility	Owing to the non-toxic biomolecule-based structural composition of the hydrogels most of them can be used for tissue engineering, biomedical devices etc. which fulfils the requirement of biocompatibility for interfacing with the human body.
Bifunctionality	Biological soft tissues and hydrogels are water-based polymeric network systems, and a broad range of biologically active functional groups can be used as constituents of hydrogels.

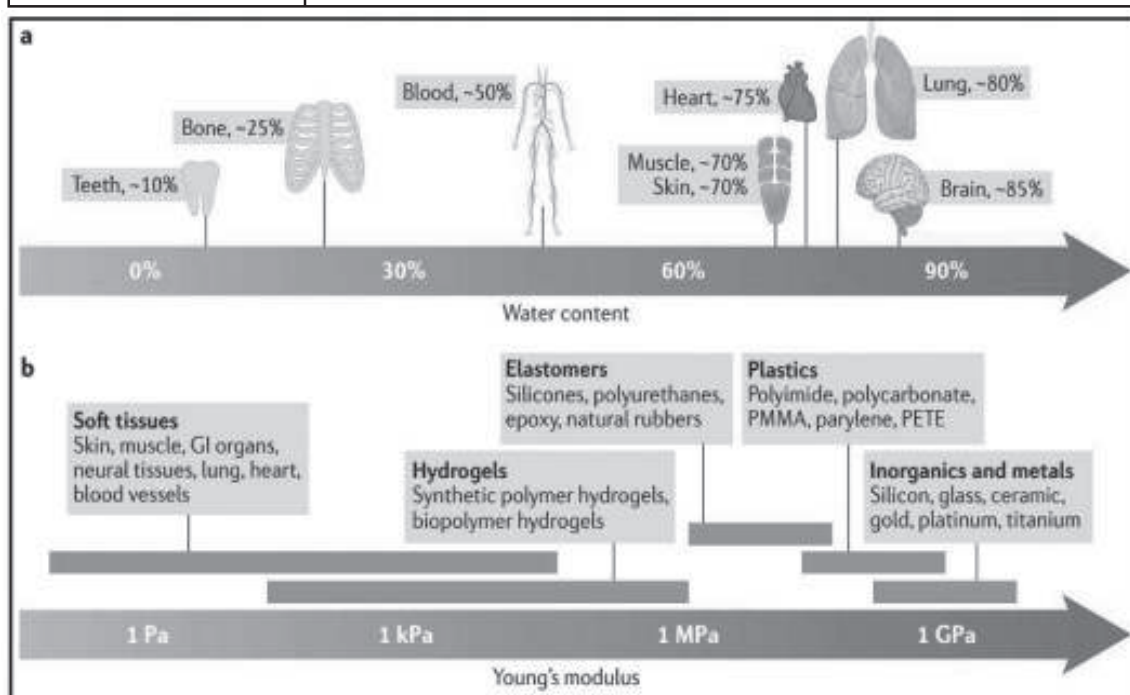


Fig 1: a. Amount of water content of different parts of body b. the scale of magnitude of Young's moduli for the comparison of soft tissues, hydrogels and engineering materials.¹

The applications of hydrogels can be largely categorized based on their interactions with various parts of the body. Among them, conductive hydrogel interfaces are applicable for epidermal and wearable applications. For instance, there are examples of commercially available skin adhesive conductive hydrogels used in clinical bio-electronics such as electrocardiography, electromyography and electroencephalography and other bioelectrical stimulations.²

Flexible electronic hydrogel-based devices exhibit soft tissue-like mechanical properties such as excellent resistance to deformation such as tension, bending or compression can enable the conversion of these deformations into recognizable electronic signals. In

terms of biocompatibility, the synthesis of conductive hydrogels preferentially follows the in-situ polymerization of the conductive monomers and thereby showing intrinsic excellent biocompatibility.¹

As strain sensors, convert physical deformation into electronic signals, conductive hydrogels are suitable candidates using sensitivity, response time and working range as the evaluation indicators. Diverse conductive hydrogels have been reported that can be employed as a sensor for human health monitoring, including breathing, heartbeat, joint bending, expression changes etc.

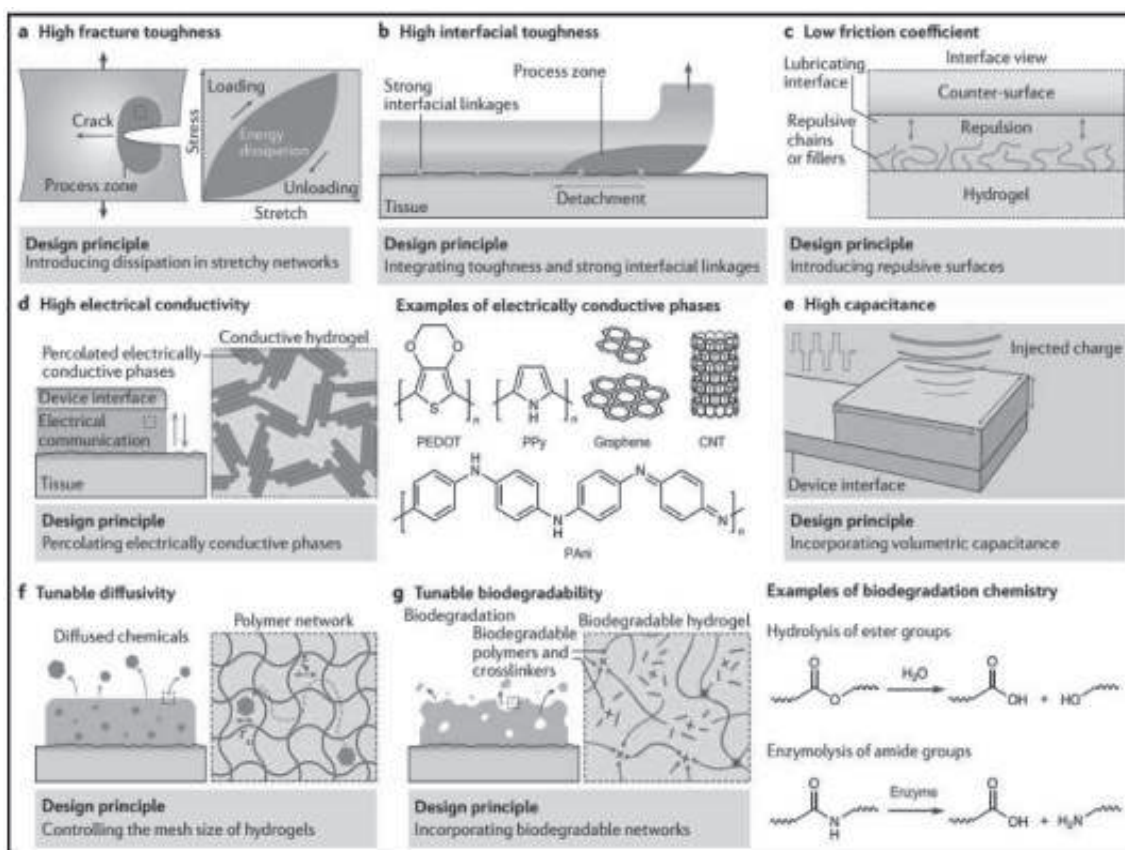


Fig 2: Design principles for hydrogel interfaces with desired properties. a. Rational design principles to achieve desired properties for hydrogel interfaces, including mechanical properties such as high fracture toughness, b. high interfacial toughness c. low friction coefficient d. electrical properties such as high electrical conductivity e. high capacitance f. chemical properties such as tunable diffusivity g. tunable biodegradability.¹

Alshareef *et al.* developed an MXene-based conductive hydrogel which is highly sensitive, stretchable as well as capable of adhering to the skin and preferably self-healing where the MXene nanosheets significantly improve the strain sensitivity of the hydrogel. The hydrogel can be attached to various parts of the body and it can significantly detect the

motions and movements of hands as well as the facile expressions by simply attaching the hydrogel to the middle of the forehead. The hydrogel exhibits an excellent ability to sense speed and motion with certain sensing applications.³

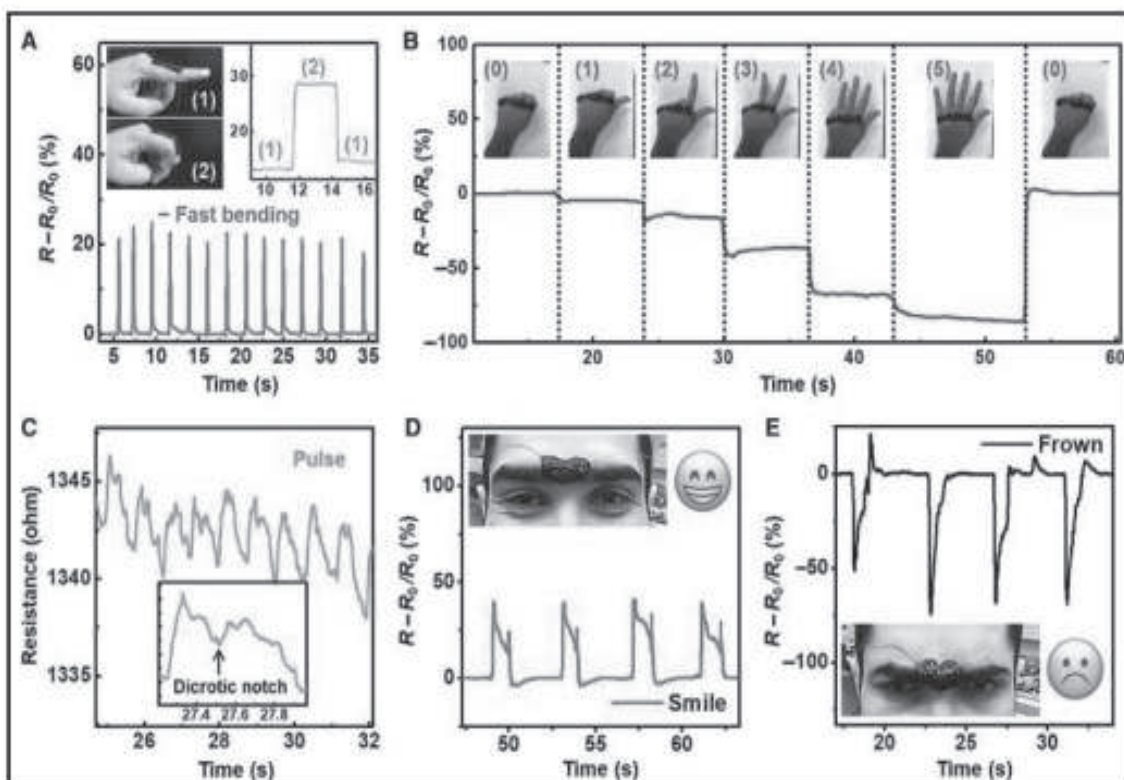


Fig 3: General sensing performance of MXene-hydrogel. (A to E) The resistance change of M-hydrogel in response to A. finger bending B. different hand gestures C. human pulse, and D. and E. facial expressions.³

Yu *et al.* reported a poly (acrylic acid)-poly (3,4-ethylene dioxythiophene) (PAA-PEDOT) with high electrical conductivity and excellent mechanical properties. This hydrogel can be used to fabricate smart epidermal flexible electronic devices for the real-time, on-body detection of various ions in human sweat.⁴ Again, recently Shi *et al.* developed a flexible electronic device fabricated from hydrogel fibres (PEDOT:PSS@PVA) showing excellent water retention and low-temperature resistance. This fibre sensor material can be used for the monitoring of complex human movements such as knuckle bending, vocalization, pulse and others.⁵

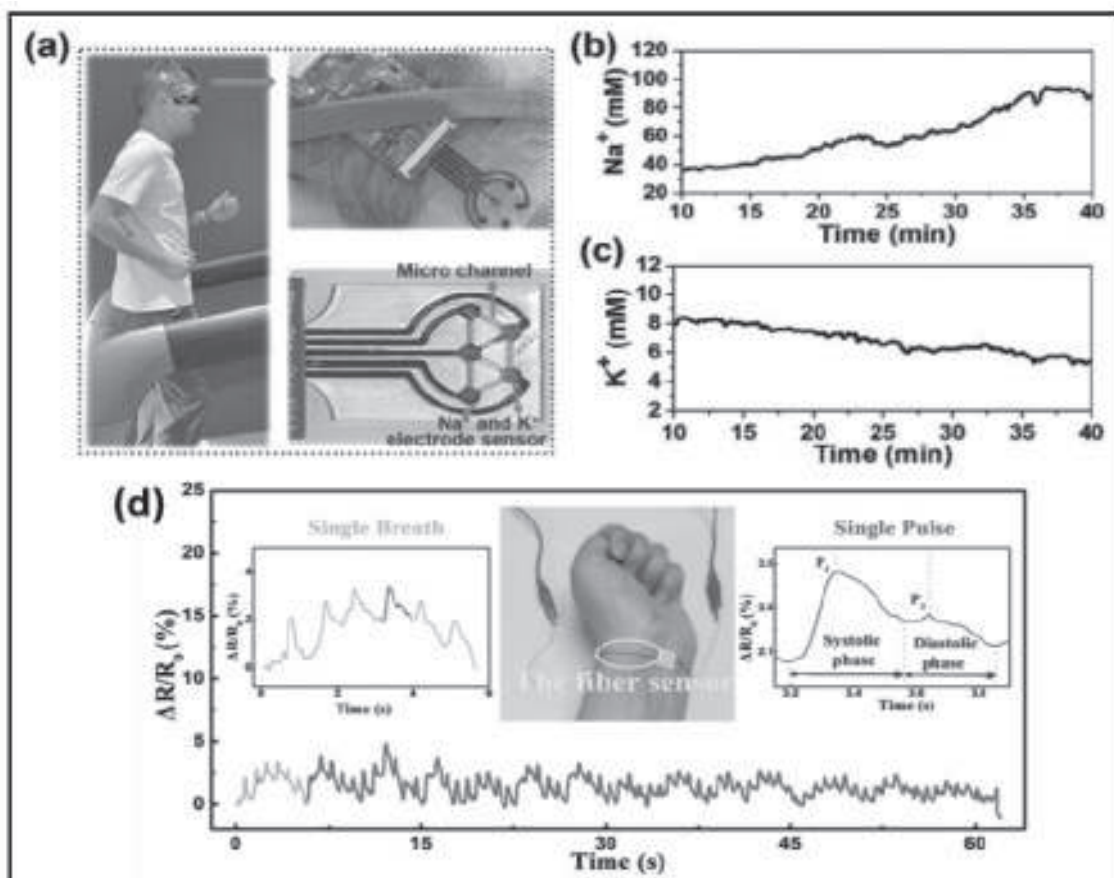


Fig 4: Real-time perspiration analysis during a running exercise. a. Photographs of a person wearing a sweat sensor during the running exercise. b. and c. The real-time data chart of the Na^+ (b) and K^+ (c) concentrations in the on-body sweat samples with the readings of the PAA PEDOT-based sensor during the running exercise. d. Respiratory and pulse signals of an adult female at rest within 1 min using the PEDOT:PSS@PVA hydrogel as a sensor.^{4,5}

The tongue is the most sensitive, soft and flexible body part of the human body containing many receptors such as taste receptors, mechanical receptors etc. Saliva and other electrolytes along with other biomolecules keep the tongue in a hydrated environment. To mimic the activity of the tongue, Yeon *et al* reported an artificial tongue fabricated from a mucin protein-derived hydrogel. In presence of hydrophobic aggregates inside the hydrogel, the formation of hierarchical micro- and nano-porous structures, facilitate the efficient transporting of ions. Because of the anti-liquid effect of hydrophobic nano-pores and reduced electrostatic interactions, Li^+ and Cl^- could flow frictionlessly through the 3D structure. To evaluate the performance in detecting astringency, a tannic acid solution was dipped on 5 different spots in a 3 x 3 array, as exhibited in Figure. below, the sensor could identify the spots precisely. The performance of this hydrogel-based sensor on the astringent sensing accelerates the opportunity of the soft materials into the bio-mimicking robot fields.⁶

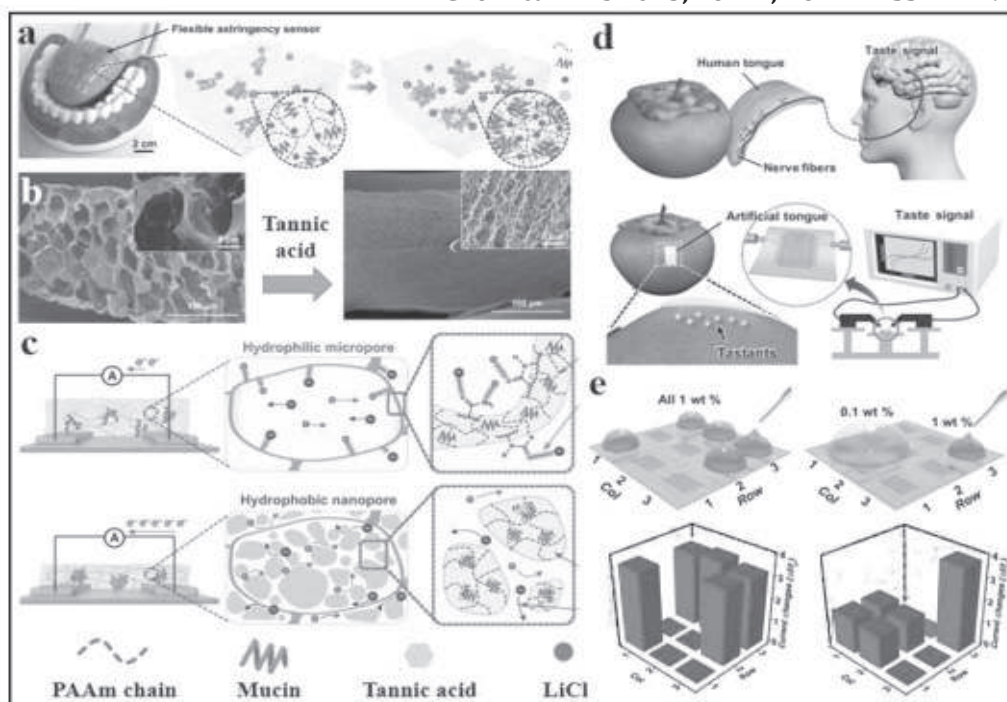


Fig 5: a. Optical photos of artificial tongue and schematic diagram of astringency sensing mechanism b. SEM image of the astringency detectable hydrogel before and after exposure to TA c. the working mechanism of the astringency sensor before and after TA treatment d. schematic representation of taste perceived by licking food e. different concentrations of TA as array artificial tongue and corresponding taste mapping data.⁶

Thus, from the above discussion we have seen that conductive hydrogels are enduring flourishing developments and researchers are continuously trying to mimic the biological soft tissues with these kinds of soft, flexible and exceptionally tunable smart materials. The hydrogel interfaces will play a major role in the near future as a merger between humans and machines and blur the boundary between the biological and abiotic systems enabling human-machine hybrids.

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■ ■ ■

Synthesis of Magnetic Nano Particles from Potato Extract: An Overview

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Abstract

The magnetic nano particles have drawing the focus of much research in recent years because they contain a numerous attractive functionality which have potential use in catalysis including nano material-based catalysts, biomedicine , micro fluidics, magnetic resonance imaging, magnetic particle imaging, data storage, environmental remediation, nano fluids, optical filters, defect sensor, magnetic cooling cation sensors etc.^{1,2} Synthesize of magnetic nano particles using plant derived potato-extract have drawn a severe attention due to their synthesis as green reaction medium. Moreover, extracted nano particles have been employed in useful application like successful dye degradation under ultrasonic radiation.

Key Words: Catalyst, Green chemistry, Nano technology, Potato extract.

Introduction

The utilization of metal oxide nano particles has received much attention due to their unique properties, such as extremely small size, high surface-area-to-volume ratio, surface modifiability, excellent magnetic properties and great biocompatibility. The production of nano particles becomes little bit easier by using conventional chemical regents that are easily available in laboratory, but these are toxic and may possess bad health. Therefore, the need for environmental and safety concern is to be use of green reaction methodologies that contains biodegradability, low toxicity as well as recyclability. At the same time, magnetite nano particles produced by green reaction medium has several benefits such as cost effective, less time consuming, can be easily used for large scale synthesis and have good stability.³

In the recent years, major research has been carried out on the synthesis of magnetite nano particles using the extract of plant, fruit, fungi, yeast, bacteria etc. Among them the plant extracted nano particles have drawn significant merit due to lowering the risk of further contamination by organizing the proper cell structure and decreasing the reaction time.^{1,4}

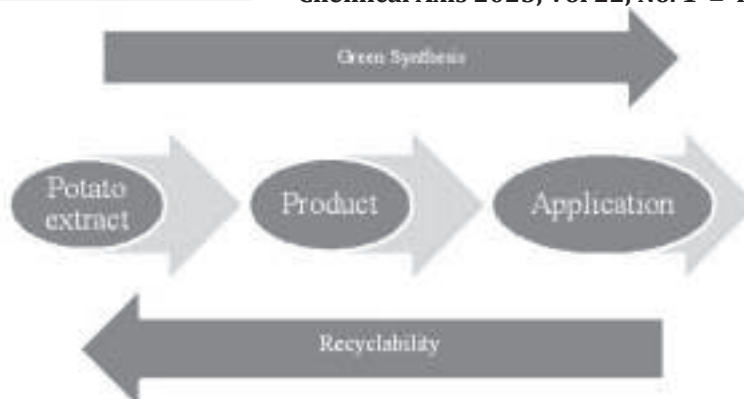


Figure: Proposed system thinking hierarchical model

The backbones of plant extracted nano particles

Plant derived nano particles has drawn the interest of much researchers due to the nano particles derived from plant extract has high stability in compare to other means and also can be easily scaled up for larger production.

G.E. Hoag *et al.* (2009) and T. Shahwan *et al.* synthesized iron nano particles using polyphenols from tea leaf extract.^{5,6} Kesarala Mohan Kumar *et al.* and Badal Kumar Mandal *et al.* (2013) synthesized iron nano particles using terminalia chebula aqueous extract.⁷ Oolong and black tea extract were used to synthesized iron nano particles by L. Huang *et al.* and Y. Kuang *et al.*^{8,9} In a study, S. Thakur *et al.*, N. Karak *et al.* (2014) studied the synthesis of iron oxide nano hybrid using banana peel ash aqueous extract as the main source and colocasia esculenta leaves aqueous extract as the reducing agents.¹⁰ In a study, E.C. Njagi *et al.* (2011) synthesized and explained biosynthesis of silver and iron oxide nano particles using rapid, single step method using aqueous sorghum bran extract.¹¹ T. Wang *et al.* and J. Lin *et al.* (2014) synthesized iron nano particles using eucalyptus leaves extract. M. Senthil *et al.* and C. Ramesh *et al.* (2012) synthesized iron nano particles using tridax procumbens leaf extract.¹²

Role of Potato extract for synthesized magnetite nano particles

The synthesis of nano particles or iron oxide nano particles using potato extract is relatively a new approach that founds a lot of success in the recent past decade due to its potentiality to design substitute, innocuous, eco-friendly and reliable modus operandi towards synthesis. The chemists are more interested to take these adequate techniques due to the unique applications of these synthesized iron oxide nano particles as catalytic materials, as adsorbents in waste water treatment, pigments, coatings, gas sensors, ion exchangers, magnetic resonance imaging, cancer cell treatment and drug delivery.

The potato is a starchy food, a tuberous crop of the plant solanum tuberosum which produces large carbohydrate contents.¹³ It contains an abundant starch, which is renewable, inexpensive and widely available in nature, present in plants in the form of semi crystalline granules. Additionally, it contains as many non-toxic biodegradable water-soluble compounds. This is the reason behind use of potato extract for the green synthesis of metal oxide nano particles in which it functions as the stabilizing as well as reducing biopolymers. By hydrolyzing the fresh starch rich potato extract, huge amount of starch and glucose can be obtained.^{14,15} Additionally, being rich in other biomolecules, the potato extract contains a numerous numbers

of functional groups like aldehydes, hydroxyl groups, carboxyl groups etc. This makes the ease for intra and intermolecular hydrogen bonding of poly-hydroxylated macromolecules to supramolecular aggregations, which works as a template for growing of the nano particles.^{3,5}

Preparation of potato extract

The amount of tuberous crop taken for the preparation of the extract depends on the required number of nano particles that are going to be synthesized by using this extract. At first the potatoes taken should be washed with distilled water several times, also the potatoes must be fresh. Then the chopped potatoes need to be sun-dried to remove the moisture and the dust particles. To prepare the extract, the dried potatoes to be taken in a beaker and boiled with water as per requirement for 15 to 20 minutes. The yellow color extract obtained are subjected to centrifuge to remove insoluble parts and the supernatant should be stored in refrigerator, which are ready to participate in the nano particles' synthesis.^{1,4}

Utilization of potato extract for synthesis of nano particles

To prepare the iron oxide nano particles, Ferrous sulfate to be mixed with yellow colored potato extract in a beaker and heat up the mixture at around 70-80°C, followed by ultrasonication. Moreover, pH of the solution should be maintained around 8, NaOH to be added drop wise for this purpose. The formation of the nano particles is confirmed by the change of color from yellow to black on addition of base on the mixture.^{1,2}

Characterization of the synthesized nano particles

The formation of nano particles can be confirmed by characterizing the synthesized crystals. Also, the demand of nano particles depends on their shape, size, morphology and magnetic behavior. Therefore, characterization is must need to study the synthesized nano particles to be further proceeding. A numbers of characterization techniques like Fourier transformation infrared spectroscopy, X-ray diffraction, energy dispersive spectroscopy, SEM, TEM, VSM etc. are used to look over their properties.¹

Use of FT-IR reveals a strong band due to the stretching of Fe-O bond, which confirms the formation of iron oxide nano particles. Other peaks obtained in the FT-IR indicate the coating of starch over magnetic nano particles. The well distinguished peak obtained in the Powder X-ray diffraction proves the crystalline behavior of magnetic nano particles. The spherical morphology of the magnetic nano particles is characterized by SEM and TEM analysis. EDS spectra confirm the various elements that are present in magnetite nano particles.¹⁻⁴

Conclusion

The synthesized nano particles have excellent magnetic properties as well as high selectivity towards targeted species.¹⁴ The highly selective nature of these nano particles renders them as highly useful in selective syntheses. A well rich performance of the synthesized magnetic nano particles plays demanding roles in recent times due to widespread applications including wastewater treatment, heavy metal removal, magnetic recording devices, magnetic data storage devices, toners and inks for electrophotography, magnetic resonance imaging, bio-separation, targeted drug delivery, pigments, flocculants, and catalytic materials.

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Aqueous Batteries: A trending technology

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Introduction:

The rising global warming and increasing CO₂ footprint drive the transformation of power generation from conventional primary fossil fuel and nuclear sources to sustainable and clean energy technologies.^{1,2} Electrochemical energy storage devices such as batteries, fuel cells, and supercapacitors play a crucial role in this area. However, the success of these systems is solely dependent on efficiency, cost, safety, and energy density. Rechargeable Li-ion batteries have found their way to grid-scale applications; however, cost and safety remain ubiquitous issues limiting large-scale applications.³ Recent incidents include Samsung Note 7 explosion (2016), Tesla Model S combustion (2019), and Ola Scooters catching fire (2022). Moreover, the progress of abundant Sodium and Potassium ion battery is impeded by safety risks and the use of environmentally challenging toxic, volatile, flammable organic electrolytes. These drawbacks of organic electrolyte-based electrochemical systems encourage exploring alternative advanced battery systems suitable for grid-scale applications.^{4,5}

Aqueous batteries are safer, economic, and sustainable alternatives than lithium, sodium or potassium ion batteries. The concept of an aqueous battery is not new to the research community. Even the first-ever electrochemical cell prepared by Alessandro Volta was assembled with Zn and Cu using sulfuric acid mixed with water. Since then, various types of primary and secondary aqueous batteries have been investigated. Some of those are summaries in Figure 1. However, aqueous batteries are not as successful as lithium-ion batteries. In this article, let's find out the merits and demerits and some strategies to improve the battery performance in aqueous electrolytes.

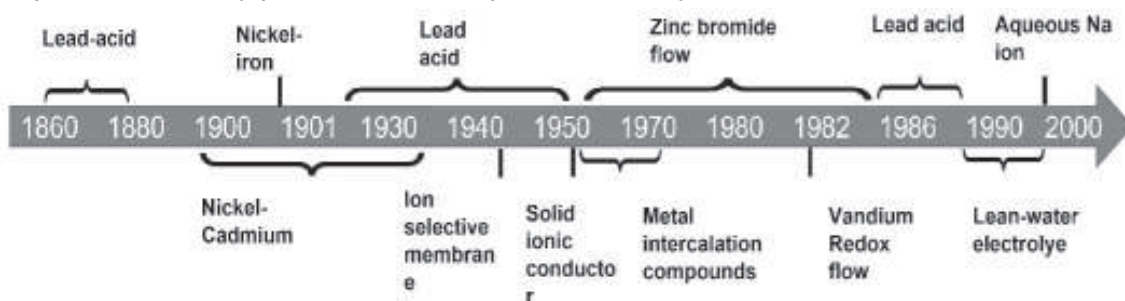


Figure 1: History of rechargeable aqueous battery.

Merits of Aqueous batteries:

- 1) **Low cost:** The cost of aqueous batteries is relatively low compared to lithium-ion battery technology. These batteries subsidy cost originates from cheap raw materials, minimal management cost, and easy battery fabrication in the open air. Using traditional salts and solutes (H_2SO_4 and KOH) contributes to the battery's low cost. However, if fluorinated salts LiPF_6 , ZnTFSI etc., and expensive additives are used, the battery's price rises. In addition, use of electrode material plays a significant role in determining the price. Manufacturing aqueous batteries doesn't require any sophisticated setup. The compatibility of these battery systems to open air eliminated the cost of moisture-sensitive materials/instruments.
- 2) **Safety:** As the aqueous batteries operate in the presence of water, the possibility of battery combustion is very low. However, if flammable solvents are added as additives or cosolvents to enhance the battery performance, they should be added in a very minimal amount.⁶
- 3) **Fast kinetics:** Aqueous electrolyte solution conductivity is higher than the non-aqueous electrolyte. This system's high ion dissociation rate and low viscosity contribute to its faster kinetics. The high conductivities of these electrolyte results in more rapid charge/discharge kinetics, smoother operation in low temperature, and less voltage polarization resulting in efficient battery performance.⁷

Challenges of Aqueous batteries:

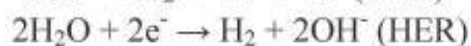
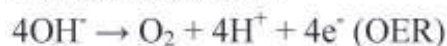
Over the last five years, this field has become very engaging, and explosive growth in the publication has been encountered. Despite having all the characteristics to become a leading candidate in electrochemical storage systems, aqueous batteries have several issues to overcome.

- 1) **Narrow electrochemical window and risk of water splitting reaction:** Hydrogen and oxygen evolution reactions are competitive in various metal ions batteries plating/stripping studies.⁸ The HER/OER reaction in the electrode surface limits the electron supply to the active material, resulting in low coulombic efficiency.⁹ Moreover, it also increases the overpotential of the system consuming lots of electrolytes.

In acidic solution:



In alkaline solution



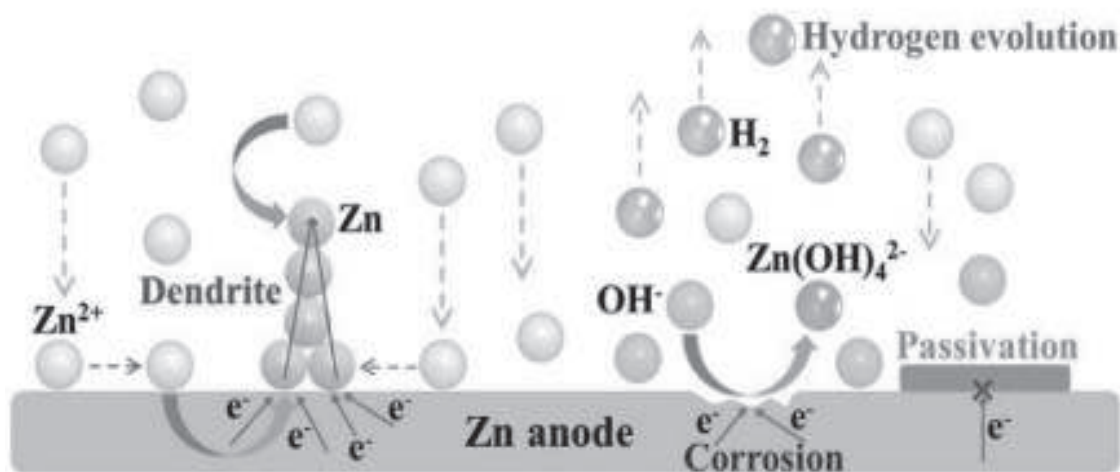


Figure 2: The challenges of Zn metal anode in aqueous system. Reprinted with permission from Ref 12. Copyright 2021 American Chemical Society.

- 2) **Dendrite Growth:** Another major problem in acidic and alkaline batteries is the formation and growth of dendrites. The dendritic growth deteriorates the coulombic efficiency and reduces the cell's cycle life.¹⁰ Apart from Zn, most other metal ions are free from this problem as the use of bare metal foil is prohibited in an aqueous solution. Zn anode is thermodynamically unstable in alkaline and mild acidic electrolytes.¹¹ In alkaline electrolytes, the Zn(OH)_2 formed at the surface of bare electrode tends to diffuse through the surface to protrusions on the electrode surface.¹² These increase the local current density at those points compared to other areas leading to uneven current distribution on the electrode resulting in dendrite formation, as shown in Figure 2.
- 3) **Passivation and corrosion:** Passivation and corrosions are never-ending problems of bare electrodes in aqueous systems. Corrosion (self-discharge) not only decreases the cell's coulombic efficiency but also leads to irreversible electrolyte consumption, resulting in increasing polarization and decreased battery cycle life.¹³

Passivation includes forming secondary insulating species such as ZnO or Zn(OH)_2 (in Zn ion battery) at the electrode surface.¹⁴ Formation of these species increases the interfacial resistance and decreases the metal ion flux toward the electrode.¹⁵ This kind of reaction occurring at the electrode/electrolyte interface plays a vital role in determining the smooth operation of a battery. So, the chemistry of the interface plays a crucial role in prohibiting these undesired reactions at the electrode surface.

Strategies to improve the battery performance:

Enormous research has been carried out to eliminate these issues. Some of these are 1) electrode interface modification 2) electrolyte design 3) proper selection of separator

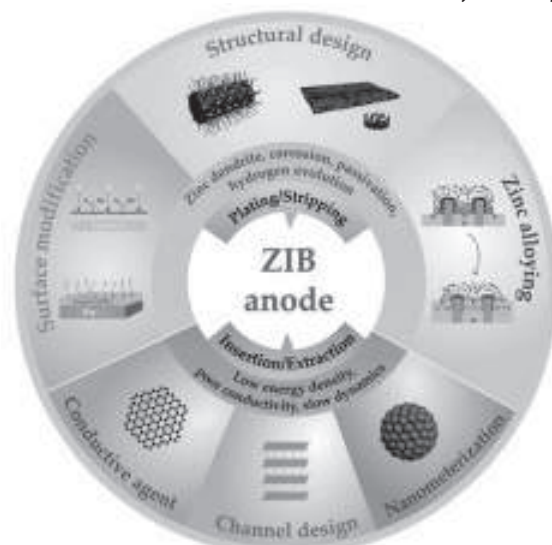


Figure 3: Strategies to increase the cyclability in Zinc ion battery. Reprinted with permission from Ref 18. Copyright 2020 American Chemical Society.

- 1) **Electrode interface modification:** One effective strategy to avoid direct contact with water with the electrode surface is building an artificial interface at the electrode surface (Figure 3).¹⁶ This layer will only permit metal ions to diffuse through it, but it will restrict the movement of H^+ and OH^- ions through the interface. Many organic and inorganic or hybrid artificial interfaces have already developed, showing tremendous suppression of parasitic reactions at the interface.^{17,18}
- 2) **Electrolyte design:** Free water molecules in the aqueous medium degrade the cathode material by dissolving the active materials and encouraging parasitic reaction at the interface.¹⁹ To suppress the water molecules' activity, modification of the ions' solvation structure is very significant. People have adopted various strategies like high-concentration electrolytes, water in the salt electrolyte, use of additives/cosolvents, etc. Though increasing the concentration and introducing additives had some success in readdressing these issues, their efficacy is being hampered by compromising key features like ionic conductivity and cost.²⁰
- 3) **Proper selection of separator:** Separators are used to keep a distance between the cathode and anode and allow ion flow between the electrodes. They should be easily wettable in an aqueous medium, electrochemically inactive, and allow easy diffusion of ions. Several studies have been performed, revealing the importance of the pore size of the separators in the growth of dendrites. The effect of various functional separators has been studied some of those are polypropylene membranes (Celgard film), polysulfonium membrane, polybenzimidazole membrane etc.^{21,22}

Summary and outlook:

Aqueous batteries are regarded as potent candidates to replace current lithium-ion technology. The key features like safety, low cost, and environmental benignity make it

more attractive to the research community. However, state-of-the-art aqueous batteries are still in its infancy. Some significant challenges are poor reversibility and self-discharge (corrosion) in the aqueous medium. Moreover, power and energy density are crucial to take to the commercial market. Significant progress has been made to uplift these technologies; however, there are miles to go before it reaches the market.

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Studying Abroad: A Broader Perspective

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"ABROAD" is merely a word which simply means "a different country" or "a foreign country" (most people likes to hear or spell out the word "foreign" rather than "different", probably because the former seems a fascinating word which brings a reflex to our mind and actions).

While thinking of writing an article of this kind, the first thought that came to my mind was "who might be the first Indian to study abroad in the 19th century?". Googling into this, I was surprised by the name that appeared, it was CORNELIA SORABJI (The first Indian female advocate, a social reformer, and writer and the first woman to study law at Oxford University. After her studies, she returned to India and got involved with several social services including the National Council for Women in India, the Federation of University Women, etc. This was the time, when India was struggling for its Independence).

We all know about the other famous personalities who studied abroad and brought major changes in building not only a "Independent nation" but also a "FREE INDIA" (however INDIA is not still free in present scenario in true sense, as it is still captured by social irregularities)

Though there are many such personalities, I would like to mention two very important leaders, without whose mention the above statement would be vague. Mahatma Gandhi: the name itself speaks a lot and it would be unfair to mention only some about him. Bhimrao Ambedkar: the most important contributor behind the India's Written Constitution. Who would have ever think that the base of the Independent India would be prepared by a "Dalit" during those days, where people revolved around inequalities.

During those days, the motive behind pursuing higher education in abroad was far more different than today's world, however exception exists everywhere. When India was at its early stage of learning (to acquire Independence), most leaders studied abroad to gain better knowledge, both in scientific and social field to deal with the British supremacy and fight against the evils of the society. In short, "Learning from abroad and investing the knowledge in their own land". However, while India changed itself from a Colony to a developing country, the people of India too changed their motive of pursuing education in abroad, with the demand for two "S" of life: "SUCCESSFUL & SETTLED".

An article in "THE HINDU" newspaper: "83% Indian students believe foreign degrees land them better jobs: Study".

This clearly indicates that students urged to study abroad than in India for better jobs which probably means "attractive salary packages". Most of them prefers to continue the rest of their life (after completion of study/ Course) in abroad too. This mentality (pursuing higher education, specially masters and PhD.) of most Indians was not built in a day. There are several factors behind this: (1) Lack of scholarship (both government and institutional) for higher studies, (2) higher level of competition (India's population: around 1.4 billion), (3) Urge to have a better life in long term, etc. Besides this, there are several factors, which pulls back the people living in abroad in returning back to their own land, mainly the feeling of "low" in terms of career and lifestyle. Moreover Indian society portrays the NRIs in a very different way. No matter how much a person achieved in his own country by facing much difficulties, he/ she will just be a USUAL and ORDINARY citizen, compared to the NRIs, who usually get a VVIP treatment from the society in terms of behavior and attitude.

It is always better to flip the other side of the coin, to check its originality. Likewise pursuing higher education in abroad (especially PhD, a long term, difficult yet interesting process) is not always seems a "FAIRYTALE", rather it is like any other decision which carries both PROS and CONS.

PROS: All the good things.

Better decent scholarship: As, English has become a global mode of communication, it is comparatively easier for Indian students to get a scholarship abroad, as most of the students pursue their preliminary and high school education (in India) in English [Thanks!! to the 200 years of colonial rule in India].

Adventure into a foreign country: While studying, students get the option to explore various countries and an opportunity to get an eye soothing view of the flora and fauna of that country.

Less time: Often we hear that pursuing a PhD in a foreign country would fetch you a "Doctoral Degree" in less than 4 or 5 years, with minimum requirements. But this is not always true in every sense. Mostly, it depends on the University as well as the Supervisor. Like, in the US, you will often hear of people finishing their PhD in 6-7 years or even more.

Higher scope of employment: The developed countries of the world, or a country with less population provides a better and easy available employment, compared to India, which is densely populated and still struggling to become a developed nation.

CONS: It isn't all good

Homesick for a long time: Most youths enjoys their freedom of staying away from home and restrictions and usually found the second home in their new friends/colleagues, etc. This feeling is very natural but short-lived. Only a person who is staying away from the family for a long time can understand that no matter how much good friends/ colleagues you have, "NO Individual can ever replace the feeling of family, except the family itself".

And after the outbreak of Covid-19, no one actually knows when there will be a sudden pandemic again, and restrictions in travel may arise for longer duration.

Language barrier: Language can either act as a bridge or as a barrier. There are many countries in the world, where natives do not understand English, and due to this, students from foreign countries had to face problems in dealing with the day to day life stuffs.

Facing racism: Racism is a global issue. Educational institutes (which constitutes learned and educated professionals) also participates in the race to practice racism directly or indirectly. The intensity of racism depends on person to person.

Reputation of the Degree upon return: In India, as we all know that besides having a Phd degree, the Doctor must possess the All India Eligibility Test certificate or several other requirements which must be fulfilled (varies according to state and the type of degree) before entering into Indian Universities for their career growth.

Every decision related to one's life and career is always loaded with pros and cons, but the happy fact lies not in carrying out a difficult task, but preparing ourselves to move forward with a decision which satisfies our mind not externally but internally too.

India (a developing country till date) is borne out of "200 years of colonization" and it would be unfair to expect a sudden change in a short period in its development process, unlike the other developed countries like the USA, Europe, etc. However, youths of any country are the building blocks of its development process, whether they contribute by pursuing their career in their homeland as well as overseas. We cannot expect everything from the government, unless we become an active contributor to the nation building.



Silk Protein Sericin: As a Versatile Biomaterial

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The biomaterials are proven to have enormous potential owing to their sustainability, abundance, recyclability and other exceptional properties of excellent adsorption capabilities and ease of modification. Sericin is a natural protein-based polymer originated from silkworms (traditionally called Leta), which hold the silk filaments together during silk spinning. By the process of "Degumming", sericin is separated from the cocoon. Sericin protein has 18 amino acids with a high constitute of serine ($\approx 40\%$), glycine, and aspartic acid, and most of them are hydrophilic in nature which provides a good solubility to sericin (Figure 1). Sericin originating at *Bombyx Mori* carries a group of proteins with molecular weight ranging from 24 to 400 kDa, while sericin from *Antheraea mylitta* owns three important polypeptides ranging from 70 kDa, 200 kDa, and > 200 kDa. Therefore, depending upon the morphology and amount of amino acid constituent, sericin can be divided as sericin-1, sericin-2, and sericin-3 with highly ample serine, glutamic acid, glycine, tyrosine, aspartic acid, and threonine. If sericin is considered a primary structure, it has a repeated sequence of amino acids, which can transform into a β -sheet structure. It is reported to affect the structural behaviour of sericin from random coil to β -sheet while treating under a thermal condition in the presence of the organic solvent.

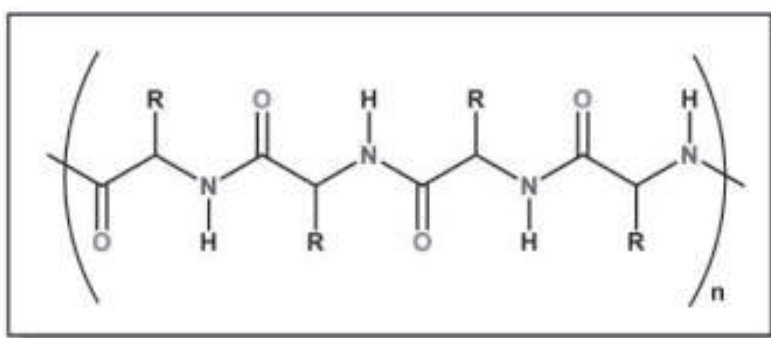


Figure1: Schematic representation of a sequence of sericin protein

Previously, sericin had been ignored as a waste product of silk degumming processes. But later, with the advances in its appraisal, it is recognised as a functional biomaterial. Due to the presence of constituent amino acids rich in specific functional groups such as

-OH, -SH, -NH₂, and -COOH, it has unique biochemical and biophysical properties and has been used for many potential applications. From the perspective of bio-resource recycling, sericin is proven to be a suitable low-cost adsorbent applicable for the removal of organic pollutants and toxic metals from wastewater. Sericin is used in the surface modification process of fibres and fabrics along with as a coating material in the cellulose fibres. It is reported that the polyester fibre modified with sericin has hygroscopic nature more than five times that of untreated polyester. Moreover, sericin with low molecular weight is applicable for cosmetics and pharmaceutical purposes. Its elasticity enhancement capacity makes it suitable for cosmetic industries. The high content of the -OH group enhances its anti-oxidant property by chelating the trace elements Cu and Fe.

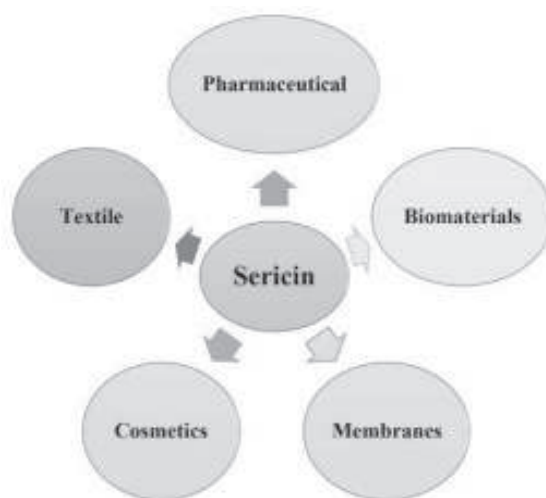


Figure 2: Field of applications of sericin.

A study is reported on an ultrafiltration process by Khosa *et al.* (2014) based on the osmotic equilibrium principle through the semipermeable membrane, which is permeable to untrapped metal ions such as Pb²⁺, Ni²⁺, Co²⁺, Cu²⁺, Zn²⁺ and impermeable to metal-sericin complex and in metal and polymeric solution (Figure 3). The silk sericin protein can act as the polydentate ligand due to the presence of different functional groups. Though both -NH₂ and -COOH group of sericin are functionally active, the -NH₂ with lone pairs of electrons is most effective for chelation. The sulfation of sericin showed its coagulant activity. Sericin matrices also found wide applications in tissue engineering. A sericin hydrogel was reported and characterized as a wound dressing. The restrictive potential of sericin in the case of UV-influenced melanogenesis was also reported. Sericin decreased the production of reactive oxygen species (ROS) and the melanin content in UV-irradiated melanocyte cells. Providing it as a highly water soluble and metal binding material, many groups have proceeded experimentally with various strategies using sericin monomer or hybrid materials of silk sericin as the adsorbent, thus unable to offer a new solution to water pollution.²⁰ These approaches allowed to outline of a variety of hybrid materials of silk sericin with desired compositions, morphologies, sizes, and structures in a greener

way using functions of organic/inorganic molecules. A key issue is to develop silk-based hybrid materials with tailored specific properties and the proper mechanistic way by which they could be able to bind heavy metals into their surface.

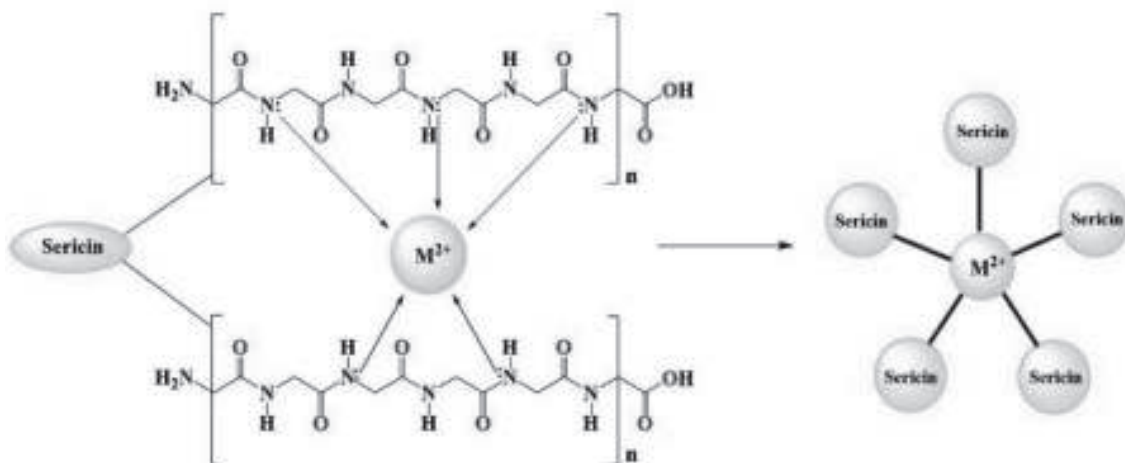


Figure 3: Formation of the metal-sericin complex during chelating interaction of metal ions with active $-NH_2$ groups of sericin.

The adsorption capacity of sericin and chitosan powder for gold was demonstrated by Chen *et al.* (2011). Biomass-derived silk sericin is cheaper, and Xinqing *et al.* (2012) used it for the removal of acidic dyes such as acid yellow (AY), Cu (II) phthalocyanine-3,4,4,4-tetrasulfonic acid (CuPc) and methylene blue (MB) dyes from water. However, the effective removal capacity of Sericin displayed over AY and CuPc adsorption but was unable to show adsorption for methylene blue dye. Because of the basicity of $-NH_2$, this selective adsorption takes place in sericin biosorbent. Gimenesa *et al.* (2016) showed that sericin powder extract from Bombyx Mori has the potential adsorption capability to adsorb Cu (II) ions from contaminated wastewater.^{7,1} Their thermodynamic and kinetics studies confirmed that the biosorption process is pseudo-second-order and exothermic in nature with monolayer interaction of Cu(II) to the polar side chains of sericin. Kwak *et al.* (2018), reported to use of beads incorporated with branched polyethyleneimine (PEI) or simply called polyhydrazine with silk sericin protein as a bio-sorbent to remove Cr (VI) from aqueous. Phenolic compounds are one of those pollutants, along with toxic metal ions, responsible for groundwater contamination. Their removal also attracted considerable attraction around the world. Abdolmaleki *et al.* (2020) synthesized functionalized graphene/sericin biomass nanocomposite to remove phenolic pollutants. The physical or chemical interaction between the functional groups of graphene with sericin mainly contributed to the process of adsorption of the phenolic groups.

Moreover, tissue engineering has also used sericin for various repair and regeneration perspectives in the form of hydrogel, films, scaffolds etc. Zhang *et al.* (2019) have developed a glutaraldehyde-cross-linked sericin nerve repairing electrical pipe to repair

nerve injury. Another approach, in this case, was contributed by Li *et al.* (2020) using a sericin-implemented carbon nanotube. Enhancing the mechanical properties of sericin using poly-vinyl alcohol Ai. *et al.* designed a wound dressing material. Recently, nanotechnology has gained tremendous attention from researchers due to its tunable size, shape, and surface characteristics as effective and potent for anti-tumour-specific therapy. Dan *et al.* (2022) have recently reported sericin nanoparticles as favourable drug delivery vehicles. Different chemotherapeutic drugs such as Paclitaxel, Atorvastatin, Inulin, Doxorubicin, Resveratrol and Fenofibrate have been taken under their study, which is successfully delivered at the targeted sites without losing the efficiency, solubility and availability in the nature.

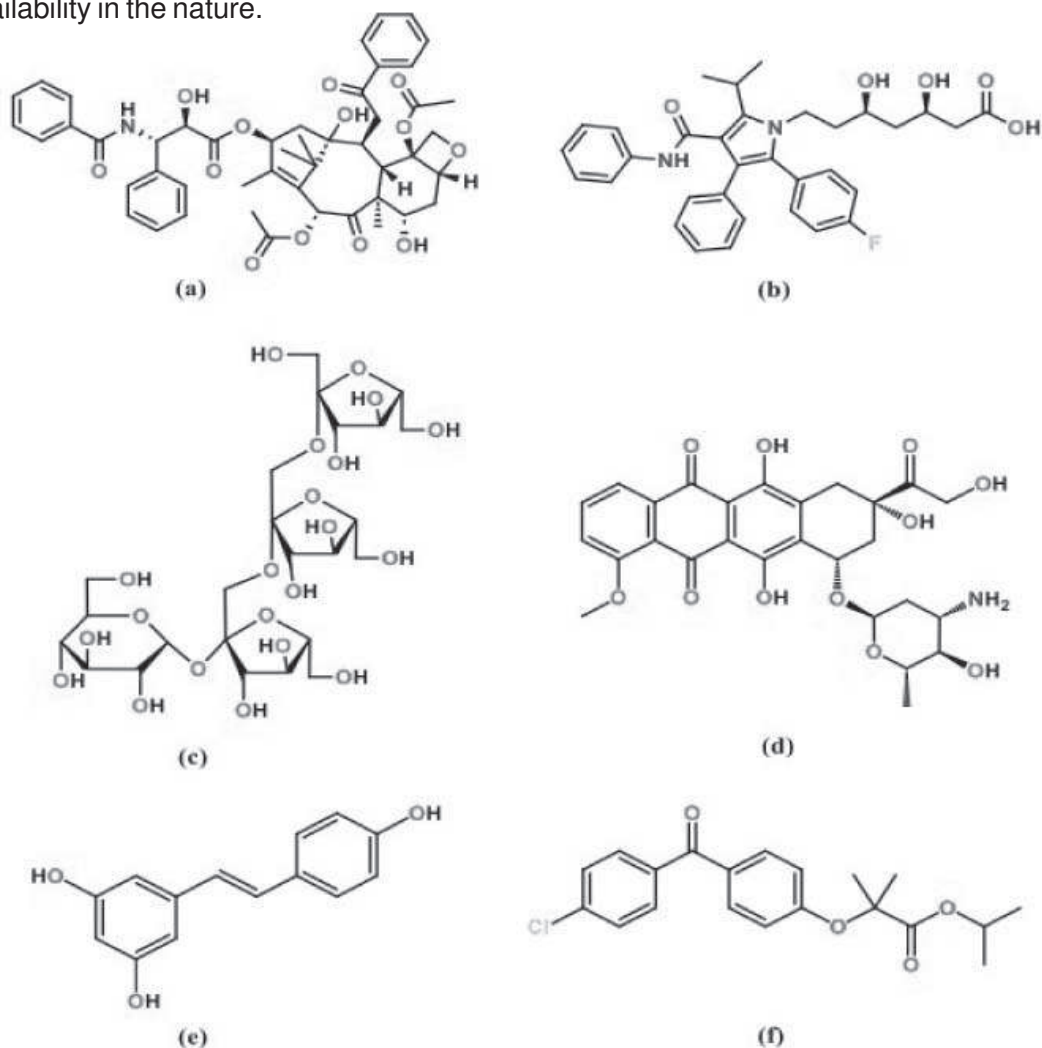


Figure 4: Chemical structure of Chemotherapeutic Drugs (a) Paclitaxel, (b) Atorvastatin, (c) Inulin, (d) Doxorubicin, (e) Resveratrol and (f) Fenofibrate

With the growing concern about the use of biologically available materials and advancement in scientific research, sericin also enhances its capability to serve as a prominent material in diverse fields, starting from the macro to the microscopical world. Though very few or zero numbers computational studies are available in the literature, with help of available, innumerable experimental reports can also provide and encourage to explore of in-depth knowledge on the boosting power of sericin.

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Graphene: the latest wonder materials of the nanoworld

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Abstract

Graphene, the one-atom thick planar sheet of sp^2 bonded carbon atoms packed in a honeycomb lattice, is considered to be the mother of all graphitic materials like fullerenes, carbon nanotubes and graphite. Graphene, the two dimensional form of graphite was first isolated in 2004 by Geim and Novoselov of Manchester University, United Kingdom. Today, graphene is the most attractive nanomaterial not only because it is the thinnest known material and the strongest material ever measured in the universe, but also due to its excellent electrical, thermal, mechanical, electronic and optical properties. It has potential applications ranging from sensors, field-effect transistors, displays, energy storage and photovoltaic devices.

Keywords: graphene, graphite, nanomaterials, micromechanical cleavage, exfoliation, polymer nanocomposites.

1. Introduction

The introduction of nanoscience and nanotechnology in the mid-90's and subsequent development of this versatile area has become prominent over recent few years, as miniaturization of both materials and devices becomes more significant in practical areas, such as computation, sensors, biomedical applications, energy storage, and many other varied applications. Nanomaterials provide an extensive collection of applications due to their structural features and interesting physicochemical properties. On the other hand, researchers are probing materials with superior physicochemical properties which are dimensionally more appropriate in the area of nanoscience and nanotechnology. By the way, the discovery of graphene and graphene-based nanocomposites particularly polymer is significant extension to novel nanomaterials. Ever since fullerene (C_{60}) was isolated in 1985 by Smalley and his co-workers,¹ quite a few novel carbon nanomaterials have been isolated. In 1991, carbon nanotube (CNT) was discovered by Japanese scientist Iijima.² On the other hand, graphene, the two dimensional form of graphite was isolated in 2004

by Geim and Novoselov of Manchester University, United Kingdom.³ Graphene has become the latest super-material in recent years due to its unique physicochemical properties such as high specific surface area, high chemical stability, high optical transmittance, high elasticity, high porosity, biocompatibility, tunable band gap and tunable properties due to easiness in chemical functionalization.^{4,5} Graphene is a flat single sheet from graphite, has the ideal two-dimensional (2D) structure with a monolayer of carbon atoms packed into a honeycomb crystal plane. Graphene is considered as the fundamental building block for graphitic materials of all other dimensions. It can be wrapped up into zero dimensional (0D) fullerenes, rolled into one dimensional (1D) nanotubes and stacked into three dimensional (3D) graphite. Therefore, graphene is called the mother of all graphitic carbon based nanomaterials. Graphene was accidentally and unexpectedly discovered by Geim and Novoselov of Manchester University in United Kingdom in 2004 from peeling off highly oriented pyrolytic graphite.³ This technique is known as micromechanical cleavage in the literature. In this technique, a cellophane tape is employed to peel off graphene layers from a graphite flake, followed by pressing the tape against a substrate such as silicon. A single sheet of graphene is obtained by removal of the tape. This is also referred as "Scotch tape" or "Peel-off" method. The existence of 2D crystal is highly controversial. Scientists Peirls and Landau had argued that 2D crystals were thermodynamically unstable and could not exist in nature.⁶ Thermal fluctuations will destroy the long-range order, causing the melting of 2D crystal lattice. It was also presumed that graphene can not exist in free state and was believed to be thermodynamically unstable with respect to the formation of curved structures such as soot, fullerenes and nanotubes. However, later it was found that the stability of 2D crystals of graphene can be attributed to the gentle crumpling in the third dimension as revealed by transmission electron microscopic (TEM) studies. A few of the outstanding physical properties of graphene has been shown in Table 1.

Table 1

Some of the amazing properties of graphene

Some basic properties	Graphene
Young's modulus	~ 1100 GPa
Fracture strength	125 GPa
Thermal Conductivity	~ 5000 Wm ⁻¹ K ⁻¹
Mobility of charge carrier	2×10 ⁵ cm ² V ⁻¹ s ⁻¹
Specific Surface area	2630 m ² g ⁻¹

These outstanding properties of graphene can be employed for the fabrication of various novel electronic devices such as field-effect transistor (FET), sensors, and supercapacitors.

2. Synthesis of graphene

Though in 2004, Novoselov and Geim synthesized graphene by micromechanical

cleavage of highly oriented pyrolytic graphite with a poor yield, several methods have been employed to produce graphene. The mechanical exfoliation method is the most primitive technique to deposit graphene monolayers and bilayers onto a hydrogen passivated Si(100) surface. On the other hand, mechanical exfoliation method has limitation in terms of its poor yield. Therefore, substitute methods are essential to produce graphene with a high yield.

The different methods which have been cited in the literature hitherto to produce graphene sheets include micromechanical cleavage of graphite, unzipping of carbon nanotubes, chemical exfoliation of graphite, solvothermal synthesis, epitaxial growth on silicon carbide (SiC) surfaces and metal surfaces, chemical vapour deposition (CVD) of hydrocarbons on metal surfaces, bottom-up organic synthesis and the reduction of graphene oxide obtained from graphite oxide by a variety of reducing agents.⁷⁻¹⁰ The last mentioned synthetic protocol gives up only chemically modified graphene. The chemical method is well known as a scalable method to attain graphene and graphene derivatives at a large scale due to its simplicity, reliability and extremely low cost. This method has been widely employed to produce chemically derived graphene. In this method, graphite is first oxidized to graphite oxide using either the Hummers method¹¹ or the modified Hummers method in the presence of strong acids and oxidants like conc H_2SO_4 and $KMnO_4$. Graphite oxide can be readily exfoliated as individual graphene oxide (GO) sheets by sonicating in aqueous medium. GO, which is an oxidized form of graphene is adorned by hydroxyl and epoxy functional groups on the hexagonal network of carbon atoms with the presence of carboxyl groups at the edges. GO is highly hydrophilic in nature and can form stable aqueous dispersions as a result of presence of large number of oxygen-containing functional groups on its surface. Chemically derived graphene can be obtained by reducing the GO using hydrazine solution or any other reducing agents.

There have been reports in the literature on the reduction of GO in solution phases using different reducing agents such as, hydrazine, dimethylhydrazine, hydroquinone, ethyleneglycol, sodium borohydride, lithium borohydride and in the vapour phase using hydrazine/hydrogen or just by thermal annealing.^{12,13} Therefore, GO is an excellent precursor to synthesize graphene nanosheets. Few-layer graphene can also be synthesized using sugars such as glucose, fructose and sucrose as the reducing agents.¹⁴ Microwave, laser, plasmas, sonochemical, electrochemical as well as hydrothermal techniques were also employed to synthesize graphene from GO.^{15,16} Table 2 illustrates the various synthetic protocols employed for the synthesis of graphene.

Table 2

Various methods employed for the synthesis of graphene

Synthetic protocol	Yield
Micromechanical cleavage (Scotch-tape method)	low
Unzipping of carbon nanotubes (mechanical and electrochemical unzipping)	moderate

Chemical exfoliation of graphite (graphite intercalation compound)	moderate
Solvothermal synthesis	moderate
Bottom-up organic synthesis	high
Liquid-phase exfoliation of graphite	high
Chemical vapour deposition (CVD)	high
Thermal decomposition of SiC	high
Chemical reduction of graphene oxide obtained from graphite oxide by various reducing agents	high
Microwave, laser, plasmas, sonochemical, hydrothermal and photochemical techniques	moderate
Electrochemical method	high
Ionic liquid assisted electrochemical synthetic protocol	moderate

3. Applications of graphene

The most significant application for graphene and graphene derivatives is most probable its use in composite materials. In fact, it has been demonstrated that by dispersing a small amount of graphene throughout polymers, tough lightweight materials can be designed and fabricated. These fabricated composites have good electrical and thermal conductivity and can endure much higher temperatures compare to normal polymers. In recent times, research group at Northwestern University, USA synthesized graphene-based polymer composite materials. These graphene-based polymer composite materials could be ideal to develop lightweight gasoline tanks and plastic containers and can be potentially utilized to build lighter, more fuel-efficient aircraft and car parts, stronger wind turbines, medical implants and sports equipments.

Graphene powders are used in electric batteries due to the high surface-to-volume ratio and high conductivity provided by graphene powder leading to the enhancement in the overall efficiency of modern batteries.

High conductivity and high optical transparency makes graphene suitable for fabricating transparent conducting coating in LCDs and solar cells. Recently, researchers from Korea and USA developed ultraviolet (UV) nitride light-emitting diode which uses a few layer of graphene as a transparent conducting layer.

4. Summary

The isolation of graphene in 2004 has brought a flow of interest in research activities as well as practical applications globally due to its unique material properties. The uniqueness in electronic, mechanical and thermal properties of graphene and its derivatives in conjunction with its cost-effective mass production build it a potential wonder material for

composites with different polymers, metals, metal oxides, and other carbon based nanomaterials. With a huge number of papers being cited in the literature in recent times, this extraordinary development forecasts an explosion in graphene research and development across the whole world. Numerous efforts have been made to further boost the properties of nanocomposites by varying the chemical structure of graphene and its derivatives through chemical functionalization. Production of solar energy directly from sunlight by using the graphene-based nanocomposites has not been achieved so far in laboratories. Therefore, generation of renewable energies like solar and wind energy and the storage of such energies in a well planned manner provide challenges in the development of various graphene-based nanocomposites.

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Foldamer: An approach to mimic Natural Higher Ordered Structure

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Introduction

Nature has chosen folding to manage the shape of its molecular machinery and perform unrivalled chemical operations like enzyme catalysis, information storage and duplication in nucleic acids, and energy collection and conversion. The link between folding and function in proteins has long piqued the interest of molecular biologists. Nature employs a somewhat restricted collection of building pieces with unique capacities to impart well-defined folds, such as twenty amino acids in proteins and four nucleobases in DNA. These building blocks evolved not just because they were well adapted but also because they met evolutionary limitations, most notably the initial requirement to be within a few steps of primordial molecules.

Foldamers are unnatural oligomers that display conformational propensities akin to those of proteins and nucleic acids, the oligomers that play starring roles in living systems.¹ Foldamer investigations frequently start with an effort to ascertain whether a particular family of oligomers has any inclination to adopt specific shapes, as many of these activities appear to need precise spatial placement of important functional groups. Proteins may perform a remarkable variety of tasks thanks to the interaction between α -amino acid residue sequence and the three-dimensional organisation of these subunits that occurs from adopting a certain conformation. Foldamers may be created in a wide variety of settings, such as the stepwise synthesis of folded oligomers, the construction of synthetic polymers, or the controlled evolution of artificial nucleic acids or protein sequences. Nevertheless, they are all part of the same initiative to mimic the characteristics of biopolymers in synthetic systems. The present impetus in foldamer research has been fuelled by a variety of causes. The first is the goal to produce someday chemical processes that are identical to those found in nature. Another crucial element is realising that chemical backbones created by stepwise synthesis, which are distinct from those of biopolymers, also adopt well-defined folded conformations. The area has rapidly developed over the past two decades, moving from early work on peptidomimetics and nucleic acid analogues to a organized investigation of folding in a wide variety of structures.

Diverse backbones and less diverse structures

There are far too many synthetic foldamers to list or even attempt to discuss all here. Many nucleic acid analogues and peptide analogues have already been successfully created to replicate the structures and, maybe, the biological features of their native counterparts before the term "foldamer" was coined. Peptide nucleic acids (PNAs)² and N-substituted oligoglycines (peptoids)³ are common examples. The wide-spread exploration

of this area triggered when Gellman and Seebach *et. al.* reported the unexpected capability of β -peptides to assume more stable helical conformations than the α -peptides.⁴ There followed investigations of b-peptides, g and d analogues as well as oligo-phenylene-ethynylenes⁵ sequences of alternating aromatic electron donors and acceptors⁶ aryl-oligomers in particular those based on aza-heterocycles (pyridines, pyrimidines, pyridazines, etc.)⁷ aromatic tertiary amide, imide or urea oligomers; and aromatic oligoamides.⁸

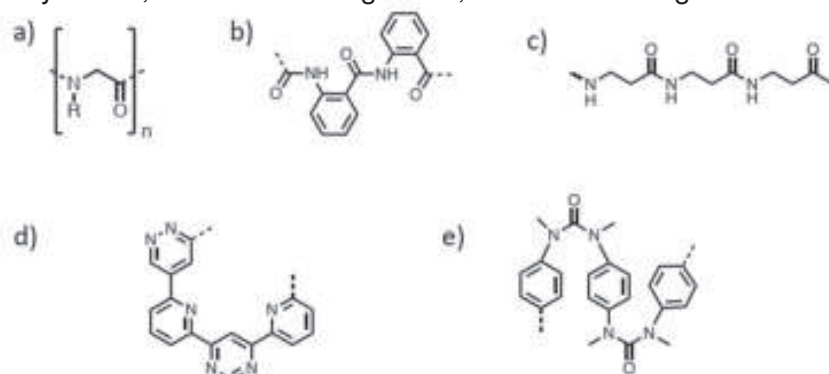


Fig. 1: Examples of foldamer backbones. (a) Peptoids. (b) Aromatic oligoamides. (c) b-Peptides (d) Aza-aromatic oligomers. (e) Tertiary aromatic ureas.

Using the secondary structures many applications has been studied but in this article, the combining sections of several natures into a single tertiary structure, such as a protein, will be discussed.

Towards synthetic foldamer proteins

Although there has been a vast number of reported backbones and the formation of secondary structures by it, contrarily, the development of artificial tertiary and quaternary folds has advanced considerably more slowly. They are more challenging to synthesise, to define, and, most importantly, there aren't many clear design guidelines for spatial arrangement of many secondary folded modules. However, the majority of the activities of biopolymers need the size and complexity of tertiary and quaternary structures. An solitary helix or sheet (secondary structures) is unable to accomplish this. Since they typically lose their secondary structure after being removed from the protein environment, the use of short α -peptide fragments to target biomacromolecules is constrained. Due to this, biological function is lost and sensitivity to circulating enzyme breakdown is raised. Thus, where peptides frequently fall short, stable protein fragment mimics may succeed. Using foldamers to replicate folded peptide segments seen in proteins, particularly the α -helix, is a novel and difficult application.

The helix bundle appears as a prevalent motif among the artificial tertiary and quaternary structures identified thus far. It is a unique protein folding pattern that has been well studied and can be produced with high levels of predictability. This advancement was considerably aided by the relatively simple crystallisation of helix bundles and the consequent availability of structural data at atomic resolution. Utilizing the knowledge from the α -helix bundles, Schepartz *et. al.* reported a 12-residue β -peptide quaternary structure (Fig 2).⁹ The structure composed of discrete no. (eight) of helices possessing a solvent excluded hydrophobic

Outline

The perspectives and expectations likewise grow as there are more successes in foldamer chemistry. In addition to offering the possibility of someday matching biopolymers in capabilities, foldamers also open the door to structures and functionalities that are not yet possible with biopolymers. A sequence's qualities may be enhanced by directed evolution iteratively and deliberately, and sequences are also susceptible to parallel synthesis and screening. With the optimised, automated chemical synthesis of lengthy peptide and nucleotide sequences as a foundation, there is no doubt that some foldamer families will soon enter a regime of regular engineering and production.

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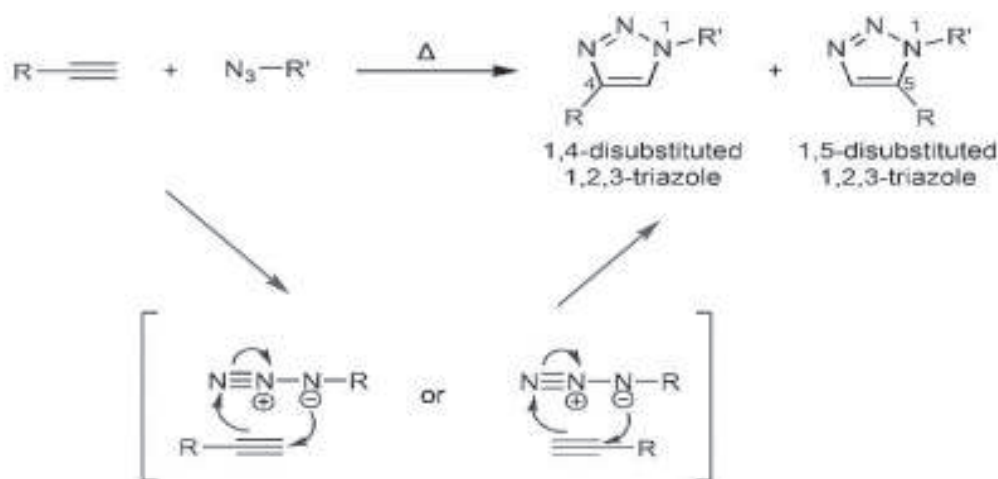


Noble Prize 2022

The noble prize in chemistry 2022, was received by Carolyn R. Bertozzi, Morten Meldal and K. Barry Sharpless for the development of Click Chemistry and Bioorthogonal Chemistry. In this article, we have tried to provide a basic understanding of these concepts and the work done by these Laureates in this direction which got them the Nobel Prize.

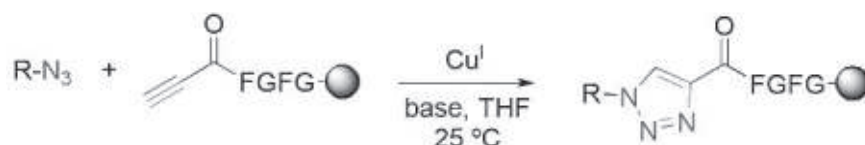
As time progresses, the way by which we perceive chemical science is becoming more and more complex. It is often a very tedious and cumbersome job to prepare complex molecules, and loads of expertise, experience is needed for perfecting these techniques. Even then, the side products generated during such complex synthesis are an another kind of nuisance. It is therefore a good thing that amid such precarious positions, we were being enlightened to simple concepts like click chemistry. The concept of click chemistry, named by Sharpless himself, is as simple as it sounds. It can be explained as making of complex molecules by clicking simple molecules together. In a formal sense, this concept entails the efficient synthesis of complex and functional molecules by using a simple approach. If we are to go for an analogy, this concept is somewhat akin to a child playing with lego blocks.

The signature reaction that has shaped click chemistry is the 1,3-Dipolar cycloaddition reaction between an azide and an alkyne/alkene.



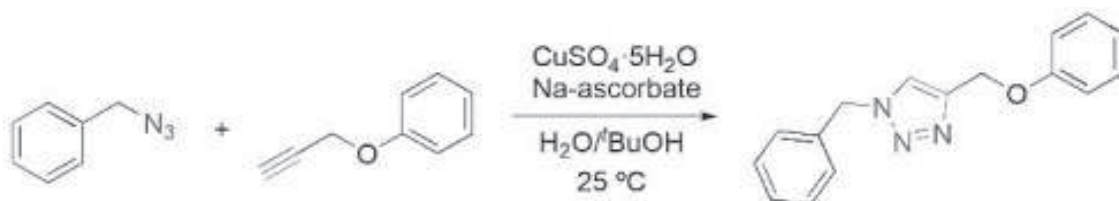
Reaction 1 : Thermally induced 1,3-dipolar cycloaddition between azides and terminal alkynes typically lead to mixtures of 1,4- and 1,5-disubstituted 1,2,3-triazoles.

But due to the slow kinetics of the reaction, the influence of the reaction was somewhat limited. But the situation changed drastically when in 2001, the catalysed reaction was discovered. In 2001, while working on the identification of efficient and mild methods to introduce the 1,2,3-triazole pharmacophore in peptides, Morten Meldal and Christian W. Tornøe discovered that Cu^I substantially catalyses the cycloaddition reaction between azide and terminal alkynes producing high yield (80-95%) of 1,4-Disubstituted-1,2,3-triazole.



Reaction 2 : Copper catalysed reaction from Meldal and co-workers; THF- Tetrahydrofuran; F- Phenylalanine; G- Glycine; • - solid support.

Independent of and in parallel with the work of Meldal, Sharpless together with Velery V. Fokin and co-workers, could also identify Cu^I as a catalyst for the 1,3-cycloaddition reaction. Almost identical with the previous reaction, Sharpless used Cu^{II} salt along with a reducing agent such as ascorbate to produce Cu^I salt in-situ. Once again, the reaction proceeded with high yield, producing only the 1,4-Disubstituted 1,2,3-triazole product.



Reaction 3 : Copper catalysed reaction from Sharpless and Co-workers.

The active copper species turned out to be a remarkable catalyst that accelerates the cycloaddition upto 107 times. Soon after, the true scale of the reaction was realised and reaction saw a dramatic upsurge across a variety of disciplines. Because of the ease of performing the reaction and inherent usefulness, the copper catalysed azide alkyne cycloaddition has become the very epitome of click chemistry becoming almost synonymous with the concept.

Carolyn R. Bertozzi took click chemistry to a whole new level. Due to the toxicity of Cu ions in biological system, the copper catalysed azide alkyne cycloaddition or 'CuAAC' was not a favourable reaction for biological system. Hence search for an alternative uncatalyzed reaction got underway and luckily it did not take long. It was found that the high strain energy of some ring molecules made them very reactive towards cycloaddition with azides. Bertozzi and team used this fact and used click reaction in biological system to tag cells in a series of bio-orthogonal reactions. Bio-orthogonal reactions are those that are able to occur under physiological conditions without interfering with, or being affected by, any surrounding biological process. Bertozzi and team took their previous knowledge

of cell engineering and incubated the modified azide-alkyne cycloaddition reaction to it. Basically, they fed cells with a modified sugar with an azide on it. The azide functional group acting as a molecule handle, expressed itself on the cell membrane of the cell as glycans (special carbohydrate located on the surface of the cell). And then in the next step, they allowed a highly strained alkyne ring that had a fluorescent green molecule attached to it to react with the cells. The alkyne then attached itself to the azide on the glycans through a click type reaction and since there was a fluorescent green molecule attached to it, the glycans on the cell surface could therefore be tracked.

The Laureates:

Caroly R. Bertozzi: She was born in 1966 in USA. She did her PhD in 1993 from U.C. Berkeley, CA, USA. She is currently a professor at Stanford University, C.A, USA and also an Investigation at Howard Hughes Medical Institute, USA.

Morten Meldal: Meldal was born in 1954 in Copenhagen, Demark. He did this PhD in 1986 from the technical university of Denmark, Lyngby, Demark. He is at present a profession at University of Copenhagen, Denmark.

K. Barry Sharpless: He was born in 1941 in Philadelphia, P.A, USA. He did his PhD in 1968 from Stanford University, C.A, USA. He is currently a profession at Scripps Research, La Jolla, CA, USA.



Outreach Program

World Food Safety Day, which is celebrated on 7th of June every year, aims to draw the attention and inspire action to help prevent, detect and manage foodborne risks, economic prosperity, agriculture, market access, tourism and sustainable development. On this occasion the Ph.D scholars along with the students of Masters and Bachelors of the department of chemistry under the guidance of Mr. Shyamal Kar demonstrated many experiments to detect the food adulterants which can be



mixed in various food items using handy reagents. The experiments were demonstrated to the students of Tarini Choudhary Girls High School, Guwahati, Assam, in a hand on fashion. The adulterants are harmful for health and responsible for various diseases. To avoid such disease, we need to know which foods are free from adulterants. The students were made aware about different types of adulterants and food colour.



On 28th of November, 2022, a **Mentoring Program** was organized for school students of different schools of Kamrup (Metro) Guwahati Assam. In the program chemistry experiments were demonstrated in an enjoyable way and in fact it was titled Chemical Magic. The aim of the program was to popularize Science subjects among the students keeping in view the low enrollment rate of students opting for science in higher studies. The experiments were performed by the Ph.D.

scholars along with the Masters and Bachelors students of department of chemistry under the guidance of Dr. Bijoy Sankar Goswami and Mr. Pradyumna Mazumdar. The students of five government school viz Rupnagar Vidyapeeth M.E. School, Lakshminath Bezbaruah M.E. School, New Guwahati Adarsha High School, New Guwahati Railway High School and Rashtra Vasha Hindi M.E. School of Assam actively participated in the program. More than 150 students attended the program.



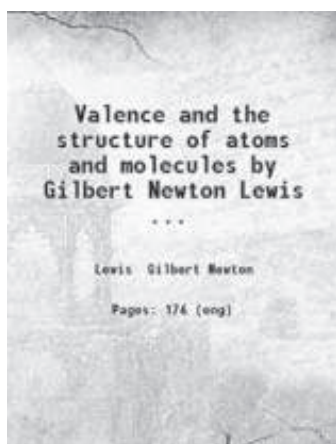
Hundred Years of The Historical Concept: The Lewis Acid and Lewis Base

Gilbert Newton Lewis, who gave this historical theory the Lewis Acid and Lewis Base, was the chemistry faculty at University of California, Berkeley from 1912, where he stayed till death in 1946. Lewis taught many graduate students, some of them became Nobel Laureates: H. C. Urey (N L, 1934) and Glenn T. Seaborg (N L, 1951).



In his life, Lewis made several fundamental contributions towards chemical science. Among those, the most important being the definition of a chemical bond arising from a shared pair of electrons between two atoms. In the early stage of his life, Lewis became interested in the nature of atoms. His notebook of 1902 contains the first formulation of his theory. But his interest was revived by the publication of a short article on the nature of bonds by W.C. Bray and the author G.E.K. Branch in 1913. This was followed almost immediately by a publication on the same subject by Lewis, and revived his ideas of 1902, which were thrown to that den of lions.

After three years this theory was published under the title of 'The Atoms and The Molecule'.



His book, 'Valence and the structure of atoms and molecules' published in 1923, which elaborated the picture of the bond and its shared pair of electrons. Lewis and his students works were directed towards the generalised concept of acids and bases at that time. In the book 'Valence and the Structure of Atoms and Molecules' Lewis proposed a very general definition of acids and bases. According to this well known definition, a basic molecule is one that has an electron pair which may enter the valence shell of another atom to consummate the electron-pair bond, and an acid molecule is one which is capable of receiving such an electron pair into the shell of one of its atom.



Shanti Swarup Bhatnagar Awardees in Chemical Science: Dr. Palliakaranai Thirumalai Narasimhan; The Twelfth Recipient

The Shanti Swarup Bhatnagar Award for Science and Technology is a science award in India given annually by the Council of Scientific and Industrial Research (CSIR). The award was instituted in 1958 with the objective to recognize conspicuously important and outstanding contribution to human knowledge and progress - fundamental and applied. The award is named after the founder director of the CSIR, Shanti Swarup Bhatnagar. It was first awarded in 1958. Any citizen of India engaged in research in any field of science and technology up to the age of 45 years is eligible for the award.



In 1970, Palliakaranai Thirumalai Narasimhan was awarded the Shanti Swarup Bhatnagar Award for Science and Technology for his contribution to chemical sciences. Narasimhan research work is in the area of chemical physics, especially quantum mechanical interpretation of magnetic resonance data for study of molecular structure and properties.

Early Life: Palliakaranai Thirumalai Narasimhan - PTN to his friends and admirers in India, Jim to his colleagues, was born in West Cuddalore, Tamil Nadu, India. He obtained Bachelors and Masters Degrees (M.Sc.) in Physics and Chemistry at Madras Christian College and earned his Ph.D. in physical chemistry at the Indian Institute of Science, Bangalore. He performed post-graduate work at the laboratory of Max T. Rogers of the Michigan State University with Martin Karplus, the recipient of Nobel Prize in Chemistry in 2013 and subsequently held faculty positions at Michigan State University, University of Illinois and Columbia University in the United States.

Academic Work: He returned to India in 1962 as one of the early faculty members at the Indian Institute of Technology, Kanpur. Over the next twenty five years, he established himself as a scientific leader and dedicated teacher in the fields of magnetic resonance and theoretical physical chemistry. He was instrumental in building IIT, Kanpur into one of

the preeminent centers of academic research in the basic sciences. After his retirement from IIT, Kanpur in 1987, Dr. Narasimhan moved to the United States and initiated a new phase of his research into novel medical and biological applications of magnetic resonance spectroscopy, first in association with the Huntington Memorial Research Institute and later at the California Institute of Technology (Caltech).

Research work:

Dr. Narasimhan has contributed to the study of principles of chemical bonding, conformation, chemical reactivity as well as electrical and magnetic properties of simple and complex molecules using molecular orbital and valence bond theoretical methods. His contribution in these areas has led to the ushering in the era of 'Computer Chemistry' in India.

Dr. Narasimhan was the pioneer in the development of dynamic nuclear polarization at X-band in India, both in terms of home-built instrumentation and chemical applications. He and his group at IIT, Kanpur developed indigenously-built phase locked super-regenerative oscillator-detectors and pulsed NQR double resonance system. The high-resolution NMR of small molecules dissolved in liquid crystalline media, and the investigation of alternating line width effects in Electron Spin Resonance (ESR) were other major undertakings of his group. His group also worked on coupling constants in NMR, spin densities and relaxation models in ESR, quadruple coupling constants employing VB and MO theories, and Sternheimer shielding and anti-shielding factors using Hartree-Fock-Slater approach.

Awards and honors:

- He was elected a Fellow of the Indian Academy of Sciences (1970).
- Fellow of the Indian National Academy of Sciences (1972).
- He also served as General Secretary of Indian National Academy of Sciences from 1977-1981.
- Fellow of the National Academy of Sciences, India (1973).
- He was awarded the prestigious Shanti Swarup Bhatnagar award in Chemical Science (1970).
- In 2009, in recognition of his services he was awarded the title of Institute Fellow by the Board of Directors of the Indian Institute of Technology, Kanpur.

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History of Chemistry

Evolution of Protein Theories (Continued)

Liebig's Analysis

Justus Liebig was a German chemist. His comprehensive survey of plant nutrition changed the nature of scientific agriculture. Liebig treated physiologic process as chemical reaction and inferred the transformations from the chemical properties of the elements and compounds in laboratory reaction.

To achieve a more definite characterization of protein, Liebig and his students verified and extended Mulder's results. Liebig analysed blood, muscle fibre and albumin and results are obtained are not much deviated from the results of Mulder. He also isolated a nitrogenous plant substance that is exactly identical to casein in composition of organic elements, proportions by weight and properties. In a letter to Wöhler he wrote,



Justus Liebig

"We have therefore a complete analogy, we have plant albumins, plant fibrin and plant casein, all three identical with each other and with the animal proteins that bear their names." (Fruton, 1972, P. 97)

Mulder has suggested a single basic 'protein' radical from which all the plant and animal substances are formed by slight modifications. Whereas Liebig postulated that a preformed plant substance that is received through diet by animals equivalents to their each nitrogenous constituent of the blood and tissues. To be assimilated, he believed these proteins required only minor alterations in form, not changes in their compositions. Sugar, fat and albumin would always originate in plants because animals might modify but were believed incapable of synthesizing compounds of this complexity.

Mulder's conflict with Liebig

The protein theory of Mulder suffered setback when Liebig and his students were unable to isolate the hypothetical protein radical free of sugar and phosphorous, even after repeating Mulder's own methods. Liebig found that a solution of fibrin in hydrochloric acid when

predicted by ammonium carbonate still contained sulfur, and that proteins similarly treated also contained sulfur. But according to Mulder's theory, the albuminous substances are compounds of differing quantities of sulfur and phosphorous with an organic radical nucleus or root substance, which he called 'Protein'. That's why according to Mulder the sulfur and phosphorus should be displaced, it should have been only protein oxide. In 1845 Liebig wrote to Wöhler, "It is a source of despair to have to see that there is no such thing as protein."

In June 1846, one of Liebig's students, Nicholas Laskowski showed that Mulder's protein hypothesis was not based on the experimental facts. According to him sulfur free proteins cannot be isolated by simple double decomposition reaction as specified by Mulder.

In 1847, Liebig dismissed the protein theory as being supported by erroneous observation and misinterpreted significance and blamed Mulder completely for the false direction followed by animal chemistry for the previous 10 years. In addition he charged that Mulder's theory had spread a false belief among the people that the nutrients are assimilated without a chemical change. Whereas in 1841, Liebig had praised Mulder's work as the most remarkable and interesting. Liebig's repudiation of Mulder's "Protein hypothesis", and Mulder's defense of it, was one of the most distressing incidents in either of their lives and revealed an aggressive and uncompromising side to Liebig's character.

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Experimental

Electrophilicity of Carbonyl Carbon Atoms of Different Organic Compounds: A DFT Study

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Introduction

Electrophilicity is a reactivity property, which defines the tendency of nucleophile attack towards the electrophilic site. In other (simple) words it is the local electron density of the electrophilic site.

Chemical reactivity property, "Electrophilicity" is an important chemical concept. In this work density functional theory (DFT) is used to calculate the electrophilicity. DFT provides a sound basis for the development of computational strategies for obtaining information about the energetics, structure and properties of atoms and molecules at much lower costs than traditional ab initio wave function technique.

Computational details

All calculation were done using the Gaussian 09 software package. Geometries of all the systems were optimized using B3LYP functional and 6-31G as a basis set.

The population analysis were performed by the natural bond orbital(NBO) method at B3LYP/6-31G++G(d, p) level of theory using the NBO program under the Gaussian 09 software.

The electrophilicity values are calculated by putting the results obtained from Gaussian 09 software in UCA Fukui software.

Results and discussion

The electrophilicity of various optimized aromatic carbonyl compound's structures are depicted in the Table - 1.

S. No	Name of Compound	Electrophilicity
1.	1-(2,4,6-Trinitrophenyl)ethanone	10.2303
2.	1-(2,4,6-Trinitrophenyl)propan-1-one	10.1773
3.	1-(2,6-Dinirophenyl)ethanone	9.002
4.	1-(2,6-Dinitrophenyl)propan-1-one	8.8591
5.	1-(2,4-Dinitrophenyl)propan-1-one	8.682

6.	1-(2,4-Dinitrophenyl)ethanone	8.6306
7.	1-(3,5-Dinitrophenyl)ethanone	8.2479
8.	1-(3,5-Dinitrophenyl)propan-1-one	8.2213
9.	1-(2-Nitrophenyl)propan-1-one	7.4227
10.	1-(2-Nitrophenyl)ethanone	7.3561
11.	1-(3-Nitrophenyl)ethanone	7.0931
12.	1-(2,3-Dinitrophenyl)ethanone	7.0686
13.	1-(4-Nitrophenyl)propan-1-one	6.9231
14.	1-(4-Nitrophenyl)ethanone	6.8987
15.	1-(3-Nitrophenyl)propan-1-one	6.6407
16.	1-(2,3-Dinitrophenyl)propan-1-one	6.4226
17.	1-(3,4-Dinitrophenyl)propan-1-one	5.5839
18.	1-(3,4-Dinitrophenyl)ethanone	5.5604
19.	1-Phenylethanone	0.9156
20.	1-Phenylpropan-1-one	0.8899

Table : Electrophilicity of various carbonyl compounds.

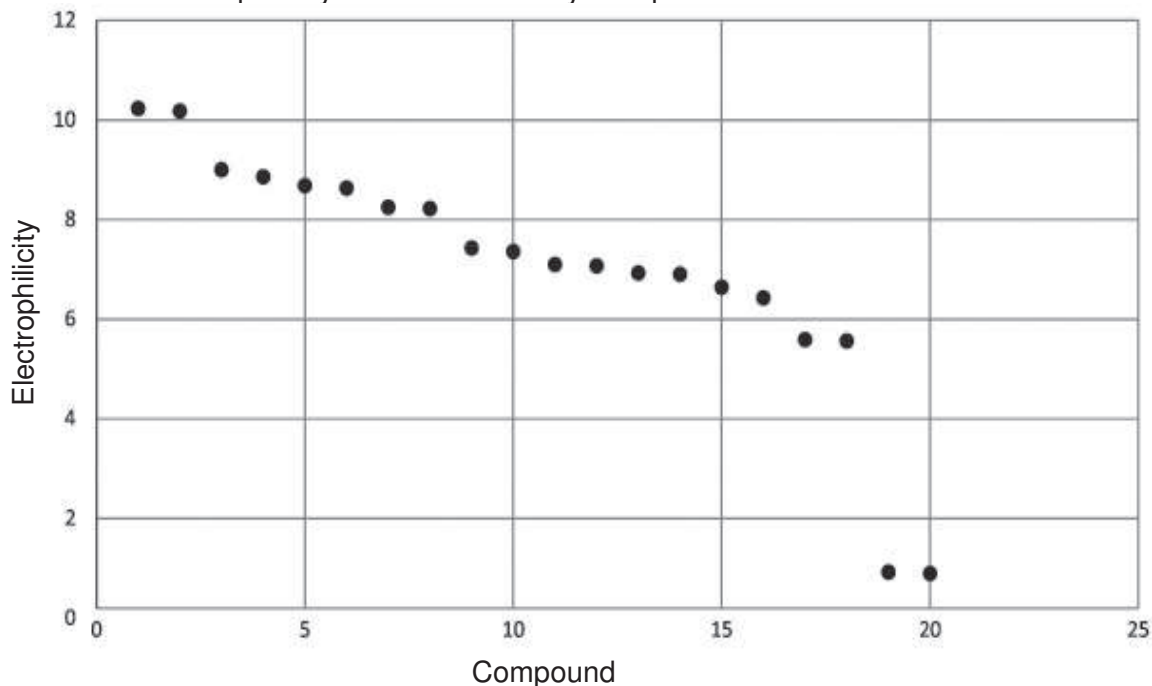


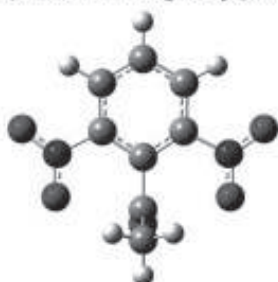
Fig. 1 : Graph showing electrophilicity of various carbonyl compounds.



1-(2,4,6-Trinitrophenyl)ethanone



1-(2,4,6-Trinitrophenyl)propan-1-one



1-(2,6-Dinitrophenyl)ethanone



1-(2,6-Dinitrophenyl)propan-1-one



1-(2,4-Dinitrophenyl)propan-1-one



1-(2,4-Dinitrophenyl)ethanone



1-(3,5-Dinitrophenyl)ethanone



1-(3,5-Dinitrophenyl)propan-1-one



1-(2-Nitrophenyl)propan-1-one



1-(2-Nitrophenyl)ethanone



1-(3-Nitrophenyl)ethanone



1-(2,3-Dinitrophenyl)ethanone



1-(4-Nitrophenyl)propan-1-one



1-(4-Nitrophenyl)ethanone



1-(3-Nitrophenyl)propan-1-one



1-(2,3-Dinitrophenyl)propan-1-one



1-(3,4-Dinitrophenyl)propan-1-one



1-(3,4-Dinitrophenyl)ethanone



1-Phenylethanone



1-Phenylpropan-1-one

Fig. 2 : Figure showing optimized structures of various carbonyl compounds

From the table we can correlate the electrophilicity and reactivity of various carbonyl compounds towards nucleophilic addition reaction.

From the electrophilicity values the following facts emerge,

- a) Electrophilicity of all the nitro, dinitro, trinitro substituted carbonyl compound is greater than the 1-phenylethanone and 1-phenylpropan-1-one. This can be attributed to the electron withdrawing inductive effect of the nitro group, which reduces the electron density on the carbonyl carbon.
- b) The electrophilicity of dinitro substituted carbonyl compounds depends on the position of the nitro group.

The electrophilicity order is found to be,

ortho-ortho > ortho-para > meta-meta > ortho-meta > meta-para

This order can be explained by the fact that nitro group at the ortho and para position can withdraw electron by resonance effect from the carbonyl carbon to a same extent. But the ortho substituted nitro group exerts more electron withdrawing inductive effect than the meta and para substituted one.

The fact that meta-meta substituted carbonyl compound is more electrophilic than the ortho-meta substituted one is probably because of the steric effect of the ortho substituted nitro substituent on the carbonyl group.

Conclusion

In summary, in this work, we have presented a comparative study to predict electrophilicity of twenty carbonyl compounds using density functional theory (DFT). The trend observed is one expected lines based on inductive effect and resonance effect. The study of other parameter coupled with electrophilicity can be of immense help in predicting the reactivity of compounds.

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Nano-sensors in Agriculture

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In the last decade, nanotechnology has become one of the most promising technologies to revolutionize conventional agriculture and food industry. The rapid development of nanotechnology has the advantage to boost agricultural production through diagnosis and treatment of diseases, enhancing the ability of plants to absorb nutrients, combat microbial and pest infections, increase the efficiency of fertilizers and agrochemicals, reduce pollution and clean up existing pollutants. Nano-sensors can detect food components in an easy and quick manner. Linking nano-sensors with modern Information and Communication Technologies (ICTs) enables novel and online ways for different components detection accompanied with high accuracy.

Applications of nano-sensors in agriculture:

Autonomous nano-sensors are positioned throughout cultivated fields combined with GPS for absolute time and comprehensive surveying of crop progress which provides high quality and essential data, such as optimum period of planting and harvesting of crops, leading to better agronomic practices.

Utilization of nano-sensors to accurately measure the soil criterion (pH, nutrients, residual pesticides, and soil moisture), checking of pathogens and estimation of nitrogen uptake helps farmers to utilize inputs more efficiently, thus fostering sustainable agriculture. Numerous nano systems are used in smart agriculture for crop monitoring, analysis of agrochemicals, moisture and soil pH. Networks of connected nano-sensors for monitoring soil or plant conditions have ability to alert automatically according to conditions detected by sensors and therefore helps in more efficient usage of the water, fertilizers, herbicides, pesticides, insecticides etc.

Nano-sensors are used to check the period and volume of water application and agrochemical treatments based on the temporal and spatial micronutrient needs of crops. Monreal *et al.* proposed that there are cross talks between roots and microorganisms in wheat or other crops' rhizosphere which are an important part of chemical signaling networks. This concept of chemical connection is utilized to develop brilliant nano fertilizer

distribution platforms for micronutrients, such as Zn and Fe. Brilliant nano fertilizers possess nano biosensors suspended in a biopolymer that coats a coating around fertilizer bits.

Nanotechnocrates possess the ability to investigate the plant's regulation of phytohormones that are responsible for root growth and seedling organization reacting with auxin. Nanotechnology-based microelectromechanical system (MEMS) sensors possess the ability to detect and also react towards changes in temperature and moisture by utilizing microelectronic circuits.

Nano-sensors for detection of pesticides residue have several advantages such as compact designs, sensitivity, low detection range, super selectivity and fast responses. Enzyme biosensors to check the presence of pesticides is based on the computation of enzyme inhibition included in the enzymatic reaction. The optical biosensors use several sensor techniques such as resonant mirrors, SPR and waveguides for the examination of biomolecular interaction. Several biosensors have been designed to detect pesticide mixtures such as methyl parathion, parathion, fenitrothion, pirimicarb, dichlorvos and paraoxon. Some biosensors are developed on the basis of acetylcholinesterase (AChE) inhibition and chemometric result calculations utilizing artificial neural networks.

Due to its wide advantages, nano-sensors applications has potential benefits in the agricultural industry and subsequent development of nano-sensors will play a vital role in the coming days.

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Nanozymes: An Artificial Enzyme for Biosensing and Immunoassay

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Natural enzymes play vital roles in biological reactions in living systems, however some intrinsic drawbacks, such as ease of denaturation laborious preservation, high cost and difficulty of recycling, have limited their practical application. To tackle these problems, intensive effects have been denoted to developing natural enzymes alternatives called "artificial enzymes".

In 2007, Yan *et al.* showed that the inorganic nanoparticles could work like an enzyme to catalyse the oxidation of typical peroxidase substrates with H_2O_2 . Fe_3O_4 MNPs instead of horseradish peroxidase (HRP) were used in immunoassay and colorimetric analysis. Later, the term 'Nanozyme' was defined by scientist Wang representing the nanomaterial-based artificial enzyme. Especially, nanozymes with oxidoreductase like activity, such as peroxidase, oxidase and catalase, have been extensively used in biosensors, immunoassay and therapy.

A few representative nanozymes are discovered throughout the years, for example-

1. Peroxidase-like nanozymes: Peroxidase are a family of enzymes that catalyse the oxidation of the substrates by a peroxide e.g., H_2O_2 , HRP, cytochrome C peroxidase etc. Studies have reported that Fe_3O_4 MNPs could mimic the activity of HRP. To date, various nanomaterials have been demonstrated to possess the peroxidase like activity, ranging from metals, metal oxides, ad metal-organic frameworks (MOFs) to carbon based nanoparticles.

2. Antioxidant nanozymes: Superoxidase dismutase (SOD) and catalase are the important antioxidant enzymes in healthy cells to remove excess ROS. It has been found that fullerene and it's derivatives as SOD mimics possessed good neuroprotective effects. Besides, CeO_2 nanozymes exhibited attractive application in anti-oxidation, anti-inflammatory as well as promoting the growth of stem cell.

Nanozymes have shown broad range of applications. According to researches this part was divided into five sub-sections, which are-

1. Determination of H₂O₂.
2. Determination of glycose.
3. Nanozyme based biosensors to evaluate antioxidants.
4. Analysis by regulating the catalytic activities of Nanozymes.
5. Nanozymes based immunoassay.

Overall, due to the simple preservation, easy storage and separation, nanozymes especially peroxidase mimics have replaced the uses of natural enzymes gradually in the field of biosensing and immunoassay.

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Sodium-ion battery: A Replacement of Lithium-ion Battery

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Introduction:

Sodium-ion batteries are an emerging battery technology with promising cost, safety, sustainability and performance advantages over current commercialized Lithium-ion batteries. This sodium ion battery system is an energy storage system based on electrochemical reactions that occur between a positive electrode composed of sodium containing layered materials and a negative electrode that is typically made of hard carbons.

Anodes and cathodes for sodium-ion battery:

Anode and cathode materials of sodium ion batteries (SIBs) can be classified into four groups.

For anodes: a) Carbonaceous b) Alloy type c) Phosphoric anode and d) Sulphides and metal oxides.

For Cathodes: a) layered O_3 b) layered P_2 c) Polyanionic compounds and d) Prussian Blue Analogues (PBAs)

Leo *et al.* (2016) In their study found hard carbon as a promising candidate for anode materials for the vast production of sodium ion batteries (SIB). Palomers *et al.* (2012) examined phosphate-based cathode materials (i.e., $NaFePO_4$, $NaVPO_4F$, Na_2FePO_4F , $Na_3V_2(PO_4)_3$ and $Na_3V_2(PO_4)_2F_3$) in SIBs and found it a suitable candidate. Because of the inductive effect, phosphates exhibit high voltage and thermal stability. Ji *et al.* (2020) reported about the use of redox shuttle to protect the SIBs from overcharging. They developed a new redox shuttle called trisaminocyclopropeium perchlorate ($TAC.ClO_4$). $TAC.ClO_4$ exhibits some good merits like rapid diffusion rate, high solubility I redox state. Due to TAC addition, heat generation I overcharged cathodes reduced by 20%.

Electrolytes for Sodium ion batteries:

SIBs can use aqueous and no aqueous electrolyte. The electrolyte optimisation is currently primarily made by varying the constituents of the electrolyte; Na-salt(s); solvent(s), and additive(s) and their respective ratios. Each component affects the requirements above to quite different. The choice of sodium salt, that is changing the counter anion to Na^+ affects both the chemical and electrochemical stability, as well as the ionic conductivity. The strength of the cation-anion interaction is reduced down to Ca 80%, moving from Li^+ to Na^+ as a cation. There is a strong temperature dependence of the ion-pairing and thus an optimal salt concentration for a maximum conductivity ad this will thus also likely differ for SIB electrolytes when compared to LIB electrolytes.

Applications of SIBs:

Studies have shown that replacing the lithium-ion battery with corresponding sodium components yields meaningful outcomes. Extensive research supports the use of Sodium-ion batteries to meet the growing demands for clean and green energy.

Some of the well-known applications of SIBs include-

Near-term application: The use of SIBs gave already begun trials in large markets including the replacement of diesel generators in regions where no electricity and network. Specific application in these locations are community mini-grids and home solar systems.

Future applications:

1. Automobiles and Transportations:

The carbon emission reduction goal has a significant impact on transportation electrification. Therefore, cost-effective battery is a necessity in electric vehicle (EV) innovation. As EV sales are expected to grow in the coming years, sodium-ion technology is the undeniable choice for electric vehicles, including electric bikes and cars.

2. Grid-level applications:

Smart grids rely on reliable power. The intermittent power supply can impede grid functioning. Sodium-ion batteries can help optimize solar energy and wind energy to effectively meet unique grid energy storage requirements.

3. Industrial Mobility:

Sodium ion batteries can maximize asset utilization and minimize operating costs with a constant state of readiness and powerful peak power.

4. Power Backup:

Data and telecom sectors rely heavily on battery powered infrastructure and operations to drive the global economy. Sodium-ion batteries can provide on demand power to ensure a safe and seamless power supply.

Conclusion:

To build better SIBs with reference to LIBs, it is crucial to accelerate R&D by better understanding of the sodium transport phenomena at the bulk and the interfaces of anode, cathode and electrolyte, and how these impact engineering practices, performance and cost which are the key for boosting the value proposition around SIBs. However SIBs would have a significant impact in application where LIBs can be substituted or hybridised pending breakthroughs in cost, performance and technology acceptance by industry.

Reference:

1. Mengya Li; Zhijia Du; Mohammad A. Khaleel; Ilias Belharouak. Materials and engineering endeavors towards practical sodium-ion batteries. *Energy Storage Materials* **2020**, *25*, 520-536. <https://doi.org/10.1016/j.ensm.2019.09.030>.
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A new, unique covalent organic framework for use in drug delivery and clean energy

Professor Yuichi Negishi from Department of Applied Chemistry, Faculty of Science, Tokyo University of Science, Japan, and his colleagues, Dr. Saikat Das, Mr. Taishu Sekine and Ms. Haruna Mabuchi have succeeded for the first time in creating a 3D COF with scu-c topology by connecting nodes of a regular plane with nodes of a regular prism. The study has been published in ACS Applied Material and Interfaces in volume 14 issue 42 of the journal on October 17, 2022. The researchers performed a condensation reaction of two organic linkers called DPTB-Me and TAPP with different symmetries, to yield 3D COF with an scu-c net like arrangement of constituents. The team then conducted powder XRD and high-resolution transmission electron microscopy to analyse the crystal structure and properties of the synthesised 3D COF.

The researchers demonstrated that the synthesised 3D COF has excellent Hydrogen, Carbon dioxide and Methane adsorption properties that reinforces its prospects in carbo capture and clean energy applications. The team unveiled TUS- 84's drug delivery capabilities with efficient drug loading and sustained release profiles using ibuprofen, a non-steroidal anti-inflammatory drug. This facilitates the delivery of sustain concentrations of drug over a prolonged period. As a result, those frequency could be reduced, and more consistent control of long lasting, chronic pain could be possible.

A membrane-based seawater electrolyser for hydrogen generation

Electrochemical saline water electrolysis using renewable energy as input is a highly desirable and sustainable method for mass production of green hydrogen. However, its practical viability is seriously challenged by insufficient durability because of the electrode side reactions and corrosion issues arising from the complex components of seawater. Although catalyst engineering using polyanion coatings suppressed corrosion by chloride ion or creating highly selective electrocatalysts have been extensively exploited with modest success, it is still far from satisfactory practical applications.

A direct seawater electrolysis method for hydrogen production radically addresses the side reaction and corrosion problems. A demonstration system was stably operated at a current density of 250 mA/cm² for over

3,200 hours under practical application conditions without failure. This strategy realises efficient, size-flexible and scalable direct seawater electrolysis in a similar way to fresh water splitting without a notable increase operation cost, and has high potential for practical application.

Scientist create crystals that generate electricity from heat.

In the effort to efficiently convert heat into electricity, easily accessible materials from harmless raw materials open up new perspectives in the development of safe and inexpensive so called thermo-electric materials. The novel synthetic material is composed of copper, manganese, germanium and sulphur and it is produced in a rather simple process, which is explained by scientist Emmanuel Guilmeau (CNRS researcher at CRISMAT Laboratory, Caen, France). According to him, "The powders are simply mechanically alloyed by ball-milling to form a precrystallized phase, which is then densified by 600°C."

Thermoelectric materials convert heat to electricity. However, thermoelectric devices used to date make use of expensive and toxic elements such as lead and tellurium, which offer the best conversion efficiency. To find safer alternatives, Emmanuel Guilmeau and his team have turned to derivatives of natural copper based sulphide minerals, and the team has succeeded in producing a series of thermoelectric materials showing two crystal structures within the same materials. The team found that replacing a small fraction of the manganese with copper produced complex microstructures with interconnected nanodomains, defects and coherent interfaces, which affect the materials transport properties for electrons and heat. Scientist Emmanuel Guilmeau says that the novel materials produced is stable upto 400°C and he is convinced that based on this discovery, cheaper and non-toxic thermoelectric materials could be designed to replace more problematic material.



CHEMISTRY IN MOVIES

Bhopal: A Prayer For Rain

"BHOPAL: A Prayer of Rain", directed by Ravi Kumar and featuring prominent actors like Martin Sheen, Mischa Barton, Kal Penn, Rajpal Yadav, Tannishtha Chatterjee is an exceptionally great film made on one of the most controversial and disastrous incidents of our Indian history (rather world history). It is a biopic about the Bhopal gas tragedy that occurred on December 2nd, 1984. A defective tank at the Union Carbide factory in Bhopal began leaking 27 tons of deadly methyl isocyanate gas into the air which resulted in mortality of 2500-6000 and debilitating over 200,000 people. Inhabitants in the township were exposed to different degrees and there were more than 500,000 registered victims that survived the tragedy. Water entered one of the storage tanks during routine maintenance, causing an exothermic reaction that breached the tank and released the gas into the air. This film remains an

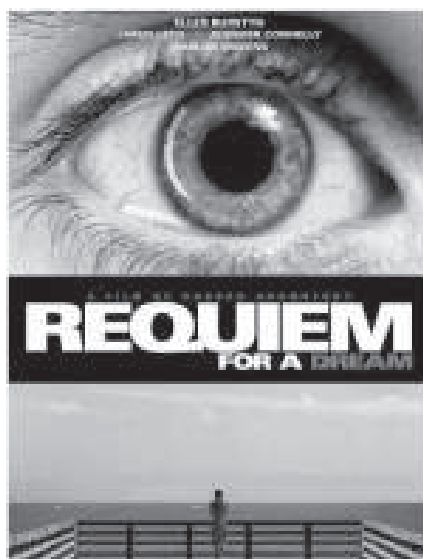


important worth watching film for its thought provoking subject and the film also makes you think about the mysterious conclusions presented by various schools of thoughts about the event's basic cause in the later years.

Requiem For A Dream

Director Darren Aronofsky's "Requiem for a Dream" revolves around the lives of four characters addicted to drugs and its adverse effects on their mental and physical health.

As the film progresses, the characters slowly dive into the world of addiction and the thin line between reality and delusion starts to blur. Of the four, one of the characters was addicted to amphetamines. Amphetamines are a subgroup of the substituted phenethylamine class of compounds. Since the mid-1990s, MDMA has become a popular entactogenic drug among the youth and quite often non-MDMA substances were sold as ecstasy. A variety of prodrugs of amphetamine and/or methamphetamine exist. Starring notable actors like Ellen Burstyn, Jared Leto, Jennifer Connelly, Christopher McDonald and Marlon Wayans this movie successfully showcases the harrowing effects of drugs all while telling the stories of all the characters.



Enola Holmes



Bringing back the cheeky and beloved young-adult iteration of the Holmes universe, Harry Bradbeer's sequel to the 2020 Netflix hit Enola Holmes, is a film that has settled into the world it is trying to create.

Despite being a work of fiction, the movie depicts the real-life industrial action that took place in 1888 by the women and girls working at a matchmaking industry popularly known as the "matchgirls' strike". The production of match sticks involved dipping the sticks, made from poplar or pine wood, into a solution made up of many ingredients including phosphorus, antimony sulphide, and potassium chlorate. Within this mixture, various proportions of allotropes of white phosphorus were also used, which caused phosphorus necrosis also known as phosphorimus chronicus or phossy jaw. The replacement of non-toxic red phosphorus by the extremely toxic white phosphorus despite being aware of its hazardous nature for commercial benefit shows the negligence towards the health of the workers. Featuring Millie Boobie Brown as the title character and other notable actors like Henry Cavill and Helena Bonham Carter, this movie makes one venture into the world of mysteries similar to one offered by the Sherlock Holmes franchise.



*I
n*

- Constructed solar panel has achieved 9% efficiency in converting water into hydrogen and oxygen mimicking a crucial step in natural photosynthesis.
- Chemical engineer's detailed a method to convert plastic waste into a highly porous form of charcoal which can potentially be added to soil to improve water retention of soil.

F

- An international team of researchers has developed a fast and economical method of converting methane ,or natural gas into liquid methanol at ambient temperature and pressure.

O

- A new enzyme variant, created by chemical engineers and scientists at the University of Texas, can break down environmental throttling plastics that typically take centuries to degrade in just a matter of hours to days.

C

- A new greener approach to synthesizing ammonia using metal organic framework (MOFs) is recently devised.

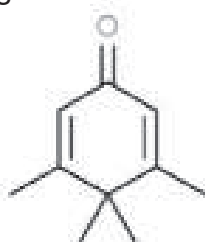
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S

- Recent studies concluded that an ultra thin polymer-based ordered membrane can efficiently remove salt from brine and seawater, offering a potential alternative for current desalination process.

AMAZING FACTS

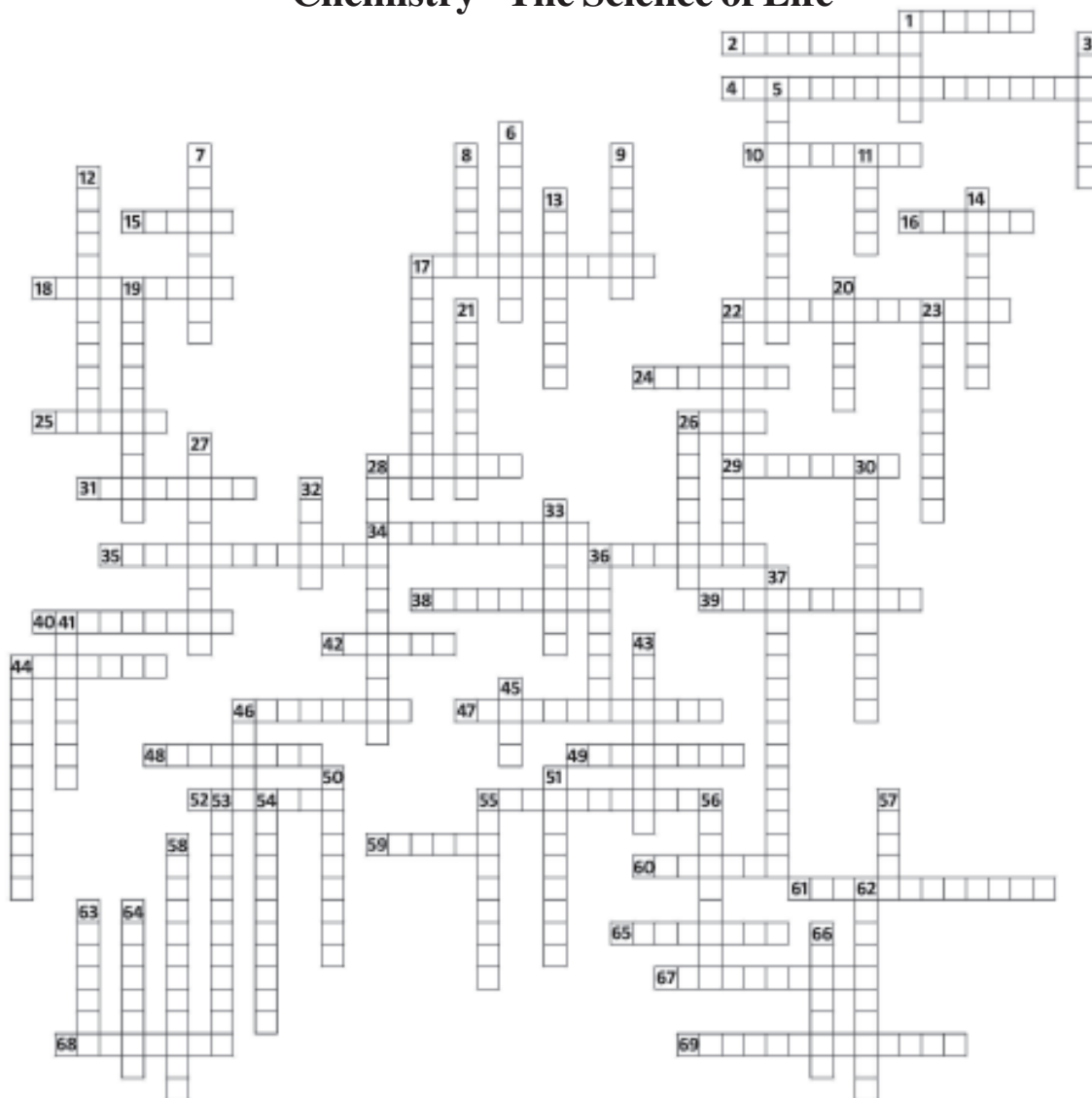
- ❖ Penguinone ($C_{10}H_{14}O$) is an organic compound and its name comes from the fact that it resembles a Penguin.



- ❖ There is about 0.4 Pound or 200 grams of salt (NaCl) in the average adult human body.
- ❖ By the time you feel thirsty, you have already lost about 1% of your body's water.
- ❖ Apple is made up of 25% of air that is why it floats in water.
- ❖ Chocolate contains phenylethylamine (PEA), the same chemical released in your brain when you fall in love.
- ❖ The letter 'J' is the only letter which is not found in periodic table.
- ❖ The amount of Carbon present in the human body could be enough to produce graphite for 9,000 pencils.
- ❖ Around 1% of the Sun's mass is oxygen.
- ❖ Rain contains vitamin B12.
- ❖ Onions make you cry due to the presence of sulphur in the cells which break after the onions are cut. The sulphur get mixed with moisture and thus irritates your eyes.

Chemistry Crossword

Chemistry - The Science of Life



Across

1. A system's ability to do work.
2. A hygroscopic substance used to sustain a state of dryness.
4. A chemical property that describes the tendency of an atom to attract a shared pair of electrons.

Down

1. R-O-R'.
3. A solid whose constituent particles are arranged in an orderly periodic microscopic structure, forming a lattice.
5. Any atom or molecule which can accept an electron pair.

10. How close a measured value is to the actual or true value.
15. A non-SI unit of measurement of electric dipole moment.
16. 1/12 of the mass of a free unexcited atom of carbon-12 at rest.
17. A solution that conducts a certain amount of electric current.
18. Interaction of a solvent with dissolved molecules.
22. Tendency of a substance to absorb moisture from the atmosphere to form aqueous solutions.
24. Glassware used to dispense specific amounts of liquid.
25. Containing at least one carbon-carbon double bond.
26. Metal oxide obtained by heating an ore in air.
28. The SI unit of electric charge.
29. General formula $R-C(H)=O$.
31. A measure of the total internal energy of a thermodynamic system.
34. Exothermic reaction that produces large amounts of heat and light.
35. Release of gas from carbonated water.
36. A substance that is made up of two or more chemically bonded elements.
38. Having an equal number of moles.
39. Acid and base.
40. Series of metallic elements with atomic numbers 89 to 103.
42. Container with a flat bottom.
44. A mixture of evenly dispersed substances.
46. The tendency of dissimilar particles or surfaces to cling to one another as a result of intermolecular forces.
47. The process by which the dispersed particles in a colloid come out of suspension to aggregate into larger clumps.
6. Any material that allows the flow of an electric current in one or more directions.
7. No water in the molecule!
8. Fully saturated acyclic hydrocarbon.
9. An intensive property of a substance defined as mass per unit volume.
11. Alkane missing a hydrogen atom.
12. The electric charge assigned to an atom in a molecule, assuming that all electrons in all bonds are shared equally between atoms.
13. Device used to measure atmospheric pressure.
14. Number of atoms present in a single molecule.
17. The condition of a system in which all competing influences are balanced.
21. The net movement of atoms or molecules from a region of higher concentration to a region of lower concentration.
22. The process of separating the components of a liquid mixture by exploiting differences in volatility.
23. A separation process in which a component is separated from its mixture by selective solubility.
26. The tendency of similar particles or surfaces to cling to one another as a result of intermolecular forces.
27. Different structural forms of the same element.
28. The quantity of a constituent of a mixture per unit quantity of the mixture.
30. Non-mirror image, non-identical stereoisomers.
32. Compounds derived from the reaction of an acid with an alcohol.
33. Molecular entity formed by loose association between two or more component molecular entities.
36. Coordination complex with carbon monoxide as a ligand.

48. A substance that increases the rate of a chemical reaction.
49. A type of colloid in which small particles of one liquid are dispersed in another liquid.
52. Containing only linear structures of atoms.
55. Molecule with both hydrophilic and hydrophobic groups.
59. A biological protein catalyst.
60. The amount of energy not available for work in a closed thermodynamic system.
61. The phase transition of a substance from a gas to a liquid.
65. Ceramic or metal dish in which substances can be subjected to very high temperatures.
67. Device used to separate substances based on size, shape, and density.
68. The mixing of air into a liquid or a solid.
69. Breakdown of a single particle or entity.
- Down**
64. Random motion of particles suspended in a liquid or a gas.
66. The process of extracting one material from another by washing with a solvent.
37. Technique for the separation of a mixture into its components.
41. The amount of energy in food.
43. A measure of a material's ability to undergo significant plastic deformation before rupturing.
44. Property of a solution that depends upon the ratio of the number of solute particles to the number of solvent particles in the solution.
45. Persistent attraction between atoms.
46. Alloy of mercury with another metal.
50. Unsaturated hydrocarbon containing at least one carbon-carbon triple bond.
51. A property of asymmetry in which a molecule and its mirror image are non superimposable.
53. The spatial arrangement of atoms affording distinction between stereoisomers which can be interconverted by rotations about single bonds.
54. Instrument used for color measurement.
55. A mixture of liquids whose chemical composition is unchanged by distillation.
56. An irreversible chemical reaction of a material, especially a metal.
57. Positive electrode.
58. The removal of ions from a solution.
62. A system in which particles of one material are distributed within a continuous phase of another material.
63. A type of glassware used in spectroscopic experiments.

This crossword is contributed by Dr. Gomathi Shridhar from
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Mumbai, India



Chemistry Puzzle

Choose the correct answer from the box given below and fill in the blanks and also find the correct answers in the grid below:

Trouton	Superfluid	Symportia	Four
Vermilion	Six	Vulcanization	Carbene
Citric	Criegee	Lactic	Betaine
Calcium			

1. Common name of Mercury sulfide _____.
2. Heating of rubber with sulfur is known as _____.
3. The bringing together of reactants into the proper spatial relationship is called _____.
4. Number of Calvin cycles required to make one molecule of glucose is _____.
5. Neutral bivalent carbon intermediates are called _____.
6. "A wide range of liquids give approximately the same enthalpy of vaporisation (about 85 JK⁻¹mol⁻¹)". This rule was given by _____.
7. The intermediate in the Bayer Villiger oxidation is _____.
8. The most abundant metal in the human body is _____.
9. A state of matter in which a matter behaves like a fluid with zero viscosity is _____.
10. _____ acid is present in sour milk.

S	O	P	E	R	T	E	E	N	C	S	U	F	A	I	M
C	V	U	L	C	A	N	I	Z	A	T	I	O	N	V	A
B	O	B	E	T	A	I	N	E	C	P	E	U	R	E	I
O	C	Y	I	F	L	R	O	G	T	S	L	R	Y	L	E
U	R	M	C	U	E	S	B	S	O	T	I	Z	G	C	N
B	I	Z	V	A	Y	Z	E	E	P	U	I	R	C	N	O
T	E	L	C	T	L	S	C	A	N	E	V	U	C	I	T
I	G	A	U	S	T	C	R	U	Y	E	S	A	X	O	U
A	E	C	V	E	R	M	I	L	I	O	N	S	U	N	O
P	E	M	I	O	L	Y	A	U	G	Z	E	P	C	S	R
U	C	R	U	T	E	B	S	Y	M	P	O	R	I	A	T
M	T	O	X	N	C	T	E	N	O	S	U	E	V	T	B
O	S	I	O	T	I	A	U	P	I	M	A	P	C	R	L
R	S	U	P	E	R	F	L	U	I	D	V	E	E	C	P
B	L	C	O	T	V	U	L	T	I	O	N	A	S	I	T
M	C	E	B	T	N	A	P	I	S	C	I	T	R	I	C

N.B. Please send the answers to The Editor, 'The Chemical Axis', Department of Chemistry, B. Borooah College, Guwahati, Assam-781007 on or before 10th February, 2023.
E-mail: thechemicalaxis@gmail.com

Any suggestion regarding the improvement of 'The Chemical Axis' will be solicited. Please send your suggestion to The Editor, 'The Chemical Axis', Department of Chemistry, B. Borooah College, Guwahati, Assam-781007.



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- ▶ *To make necessary arrangement for beneficiary programme for the students.*

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