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Happy Teachers' Day

Editorial ...

> *"Not all of us can do great things. But we can do small things with great love. Your true character is most accurately measured by how you treat those who can do 'Nothing' for you"*
>
> **- Mother Teresa**

The recent boom in technology has changed the average lifestyle of human.All manner of technology surrounds us. From our personal laptops, tablets and phones to behind-the-scene technology that furthers health and medicines, science, education etc. Technology is here to stay, but it's always morphing and expanding. As each new technology enters the scene, it has the potential to improve lives. But in some cases, it also has the negative potential to affect physical and mental health.

The adverse effect of technology on human health is uncountable. The most prominent effect of science and technology is psychological effect. A 2017 study in young adults aged 19-32 years found that people with higher social media use were more than three times as likely to feel socially isolated than those who didn't use social media as often. Depression and anxiety is the tip of iceberg of many health issues. Along with the mental health, physical health doesn't remain untouched by harmful effect of technology. Lack of sleep, eyestrain, headache, neck-shoulder pain, musculoskeletal issues, obesity, cardiovascular diseases are few examples of them. The effects of technology in children are alarming too, such as retarding growth, low mental growth, restlessness, anxiety, aggressive behaviour, obesity etc.

As we are coming the end of the year 2022, we are back with the final edition of The Chemical Axis 2022 vol.21, No.21.The motto of The Chemical Axis had always been to ignite,inspireand nurture the creative instincts of budding minds to mould them for better tomorrow. In this regards, various articles relating to the present scenario and other fields are listed.In this editions a wide array of topics have been covered such as peptoid polymers for designing hierarchical nanostructures, cancer treatment(photodynamic therapy).A highly informative pieces of theoretical chemistry is also included.

The series of bhatnagar awardees and chemistry in movies has been continued.

Date: 17-09-2022
Place: Guwahati

The abstract sketched on the cover page has been designed by ***Nazrul Islam*** *on the quotation*

"Everything is theoretically impossible, until it is done."

- Robert A Heinlein

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Quest towards a greener planet: An approach to efficient greenhouse alternatives

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IIT Guwahati, Assam, India

Somewhere in the city,

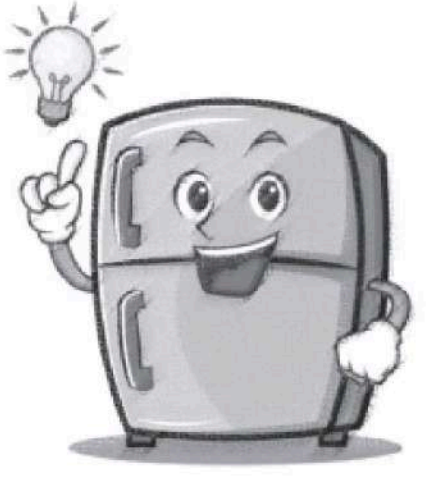
भैया एक पानी बोतल देना, ठंडा!!"

और भैया ने फ्रिज का दरवाजा खोला ...

Brother, give me a water bottle, cold!! And then the shop owner pulls one door of the refrigerator…

As a child, I was really fascinated by the fact that how a 1.5 x 0.5 m box keeps the items cool which are stuffed inside it. In the summers, I used to open the doors of the refrigerator and stand in front of it, just to beat the heat. I am sure that everyone has tried this, at least once in their life. Also, I would repeat this day after day.

Have you ever wondered what makes Refrigerators so special?? How are they able to keep COOL and CALM in the burning heat of summer?? How do they keep food products fresh??



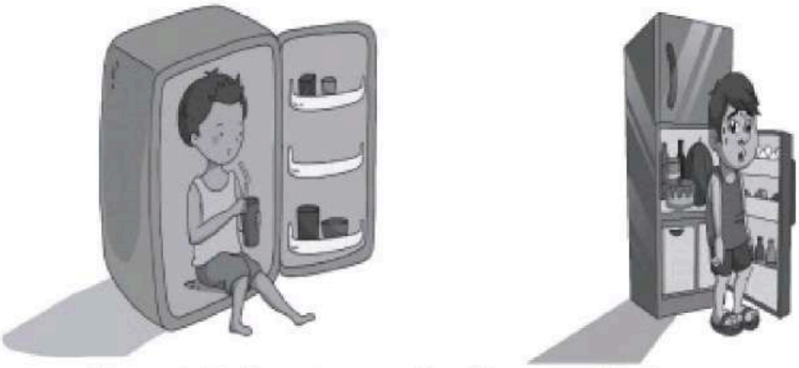


Figure 1: Refrigerators used for different applications.

Initial drive

This curiosity introduced me to the word, 'Refrigerants'. Initially, I believed these refrigerants are responsible only for the preservation of food products and keeping the temperature low in refrigerators. But it was only later that I understood that refrigerants are a class of compounds typically found in fluid or gaseous state that absorbs heat from the environment and provide Refrigeration (Artificial cooling)[1]. These refrigerants were divided into different groups on the basis of their chemical composition. One such major class of compounds which were widely used in the early 90s are the Chlorofluorocarbons (CFCs). CFCs comprises of number of volatile derivatives of hydrocarbons merged with halogenated elements like fluorine and chlorine[2]. CFCs are very harmful to the environment and in order to minimize the environmental problems allied with it, they were termed as potential threat to the atmosphere and ozone layer[3]. It was at this moment when I realized that better alternatives to CFCs urged my immediate attention as it was affecting our environment in a rapid manner.

Historical Background

Chlorofluorocarbons (CFCs) do not have any natural background. It was in the early 1930s, when an American based company hired a group of scientists to seek for a non-flammable, non-toxic and cheap alternatives to Refrigerants[3]. And they ended up synthesizing the first CFC **(dichlorodifluoromethane, CF_2Cl_2)**[4].

Thomas Midley Jr. led this group of Scientist. He was named 'the Father of CFC'. But it was only in the 1970s, when scientist found relationship between ozone layer depletion and CFCs[5,6]. CFCs were chemically very stable and this chemical stability helped them to diffuse into the stratosphere from the troposphere. The release of CFCs has a lot of impact on the global environment and this has led to some non-permanent replacement by hydro-chlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs). HCFCs do not contain any chlorine or bromine atom in them, hence do not inflict serious threats to the ozone layer. However, due to the presence of chlorine-fluorine bond(s), these HCFCs may also lead to absorption and thereby contributing highly to the global warming[7]. These CFCs replacements have hydrogen atoms incorporated to their structures to lessen the transport of chlorine-containing compounds into the stratosphere. These were better replacements as they were not only environmentally suitable but also met various commercial and industrial needs. These CFC alternatives surprisingly share many physical and chemical properties which are identical to those of CFCs.

Is it too late to realize the ill effects of Chlorofluorocarbons?

Great concerns for the depletion of the stratospheric ozone layer by anthropogenic CFCs began with the pioneering work by Molina and Rowland in 1974[5,6]. Also, For the fast recovery of stratospheric ozone layer, the International legislation mandated *the Montreal Protocol*[8] and *Kyoto Protocol*[9] to slowly dispose of the production of ozone-depleting substances (ODS).

The Montreal Protocol, 1987 was an international treaty designed to protect the ozone layer by phasing out the production of numerous substances that are responsible for ozone depletion. This was considered to be a landmark agreement that has played an important role in scaling down the global production, consumption and emissions of ozone-depleting substances (ODSs). ODSs are greenhouse gases that contributes majorly to climate change Similarly, ***The Kyoto Protocol*** can be thought of as an international treaty that seek to reduce carbon dioxide emissions and the presence of greenhouse gases (GHG) in the atmosphere. This was adopted in Kyoto, Japan in 1997 but went into force in 2005. Six greenhouse gases were included - CFC was one of them. However, there are still million and million tons of CFCs all over the world as they are significantly used as coolants in numerous air-conditioning systems. Thus, finding a practical way to diminish the CFC pollutants or prevent use of existing CFCs is of immense importance.

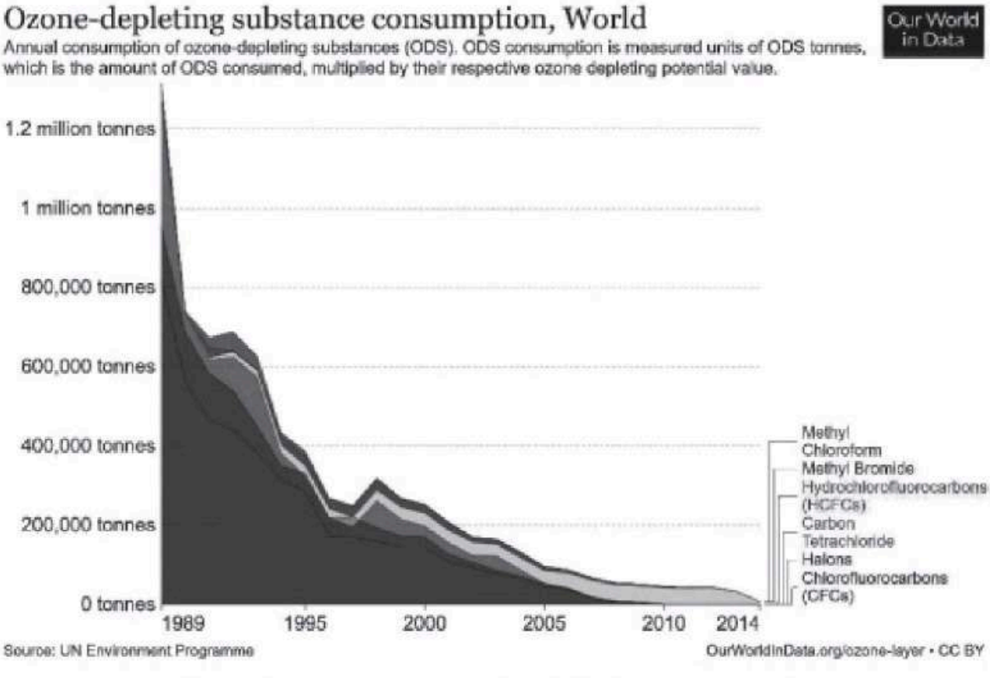


Figure 2: Decrease in the Global CFC Consumption[10].

Why this problem is of utmost concern and requires immediate interest from the researchers? What makes this most important?

Over the years, CFCs has been extensively used in many industrial processes. Its production has gradually decreased due to the decreasing demand for CFCs as proposed by Montreal protocol. We have seen that CFCs were very harmful not only to our environment but also to us as it significantly contributes to the increase in greenhouse gases. Even though the CFCs-alternatives have reduced the use of CFCs but a proper investigation regarding depletion of CFCs in the environment is of utmost importance. These are very highly stable compounds and have long life-times which are estimated to be more than 50 years[1,2]. Due to these factors that leads to the increase in concentration of the greenhouse gases in the atmosphere, Researchers across the world have been searching for new innovative ideas in an attempt to decompose CFCs using different catalysts and newer, greener approaches.

Why does the research matter?

From the studies it is seen that the damage has already been done, but the question is to what extent are we ready to go to cut down the ill effects on the environment. Our current research is based on two objectives. First, degradation of CFCs present in our environment and second, finding a good alternative (imitating most of the properties of CFCs) that tend to pose a lesser impact on the environment. The idea of degradation of CFCs and finding a good alternative is not something new and I believe that different groups across the globe have given it a shot as well but what is required now is a fresh and new approach to deal with this problem.

After extensive literature review, we concluded that it would be a great idea to degrade CFCs using radicals present in the atmosphere. However, the difficult part was radical selection because we wanted a radical that was readily available as well as widely studied. The hydroxyl radical suited our needs. Presently, we are going to design different pathways for degradation of CFCs using hydroxyl radical. Our approach will include computational studies, by mimicking the chemical reactions taking place in the atmosphere, which will be followed by analyzing those results with the help of artificial intelligence. The thermodynamics (spontaneity) and kinetic (rate of the reaction) results analyzed using computational techniques will provide us a valuable output to understand the mechanism of the reaction. We believe that this approach will not only give us a crude idea of how the reactions in the atmosphere are sought to occur but will also provide us a broad picture of how one can move forward to lower the effect of such greenhouse gases for remarkable innovations. Those days are long gone, when chemistry was only constricted to beakers, test tubes and working in laboratories but this is the beginning of a new era of computational research wherein computational techniques, artificial intelligence and the basic concepts of chemistry go hand in hand to provide us a new perspective to look at the modern day problems. Hence, I believe that computational studies using high performance computing facilities will play a vital role in development of scientific research in the near future.

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■ ■ ■

Valence Bond Theory Cannot Explain the Paramagnetism of Dioxygen Molecule: Is it True???

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[I am writing this article because we were mostly taught in the undergraduate level that the Valence Bond Theory is a dead theory, and the most prominent citing example of its failure is the mentioned title of this chapter.]

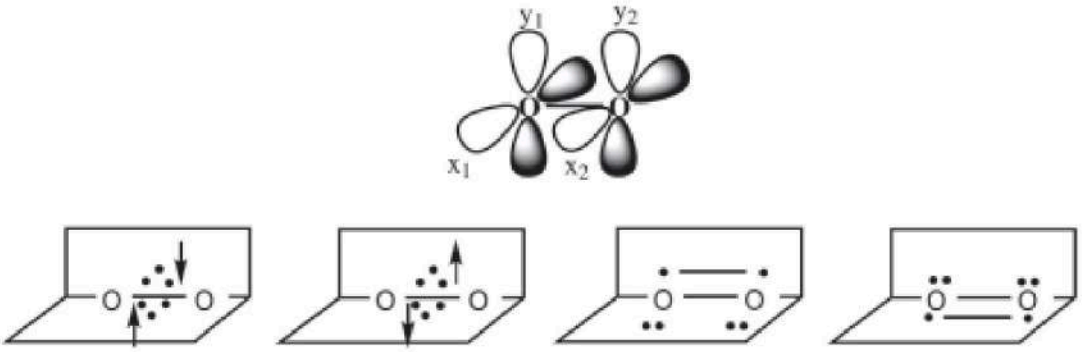
The origin of Valence Bond Theory, or VBT, can be traced back to the second decade of the twentieth century. It all began in 1916, when Lewis published his seminal paper on electronic structure theory, "The Atom and the Molecule."[1] His innovative idea of describing a chemical bond with electron dots is still used in most classrooms and is included in all common chemistry textbooks. Lewis' grand idea was first realized in quantum mechanics by Heitler and London in 1927-1928.[2–4] Linus C. Pauling, the pioneer of VB theory, was in Europe during that period, trying to learn the new quantum mechanics. Later, he moved to the United States and conceptualized the well-known VB theory, which focused on understanding the nature of chemical bonds.[5] His theory garnered widespread attention and appreciation from scientific communities, earning him the Nobel Prize in Chemistry in 1954. One of the contemporaries of Pauling, Robert S. Mulliken, developed a different theory called the Molecular Orbital Theory or MOT to explain chemical bonding, which had a spectroscopic origin.[6–9] Even though both theories attempted to understand and explain the chemical bond and its application in molecular structure, they quickly became rivals amongst their respective promoters and supporters.[10] At the present state, we all know that MOT is the most celebrated electronic structure theory and widely used everywhere viz. molecular structure prediction, electronic properties of materials, reaction mechanisms, several quantum software, and many more. However, this was not the case in 1930s to mid 1950s. Subsequently, this period saw the surge of VBT over MOT in all aspects of chemical bonding explanation. Eventually, in 1950s, a gradual downfall of VB theory started followed by a steep upheaval in the early 1960s. Then, the fall of VB theory became decisive once it ceased to guide the organic chemist to predict its structure and properties during 1960s to 1978. In the book of Shaik and Hiberty[11], they state that *"the conceptual development of VB theory was arrested since the 1950s, in part due to the insistence of Pauling himself that resonance theory was sufficient to deal with most problems. Sadly, the creator himself contributed to the downfall of his own brainchild."* After the temporary demise of VB theory, the ultimate resurgence started in the late 1970s and early 1980s and it continued with new ideas as •emodern VB theory'.[11,12]

Let us now formulate our article discussion problem. To do so, we must return to 1929, when, according to Brush[13], Lennard-Jones was the first to write the wavefunction for the MO theory.[14] He essentially attempted to discuss the bonding and electronic structure of diatomic molecules, demonstrating that dioxygen molecule is paramagnetic. Furthermore, he mentioned in his paper that the Heitler - London VB method struggled with the correct description of the dioxygen molecule. Since then, this molecule has become the most basic symbolic failure of VB theory. Nonetheless, the question arises: is this true? If we read Linus Pauling•fs seminal paper, we can see that the O_2 molecule does not exist in its normal state, but rather one with two three electron bonds.[15] Similarly, Heitler and Poschl published a Nature paper in 1934 that described the O_2 molecule using VB principles and concluded that *"the $3\Sigma_g^-$ term... giving the fundamental state of the molecule"*.[16] As such, it is unclear how the myth of this "failure" grew, spread, and got universally accepted.

It is true, if we only use hybridization followed by perfect Lewis's pairing, we all end up with the doubly bonded diamagnetic ground state of O_2 molecule. This attitude, however, is not particularly scientific, because Goddard et al. performed Generalized VB calculations in the 1970s and demonstrated that VB theory led to a triplet $3\Sigma_g^-$ ground state.[17] The same result was obtained in papers by McWeeny[18] and Harcourt[19]. Later, Shaik and Hiberty offered a straightforward VB description for the preference of O_2 ground state.[20] In reality, it can be stated that whatever VB computations are carried out at any imagined stage, will produce the same result, proving that the myth of "failure" is unjustified.

In order to form the dioxygen molecule, each oxygen atom contributes one σ and three π electrons, with the remaining pair of electrons of each oxygen localized as the σ lone pair. Thus, the dioxygen molecule has six π electrons that are distributed in two π planes, π_x and π_y (cf. Figure 1). Furthermore, this can be depicted in two possible distributions in accordance with their corresponding VB wavefunctions, as shown in Figure 1. The question is, which is the most favorable? In case 1, three electrons are assigned to each π plane, whereas in case 2, two electrons are placed to one plane and the remaining four to another. A closer look reveals that structure 1 is diradical, with one 3e bond in each of the π planes, whereas structure 2 has a singlet π bond in one π plane and a 4e repulsion in the other. At this point, if the repulsive 3e and 4e interactions are ignored, structure 2 is clearly preferred, which results in the closed shell singlet ground state structure of the O_2 molecule. This is how the mythical failure of VB theory manifests itself: it cannot adequately explain the ground state structure of an O_2 molecule.

Nevertheless, when we calculate the repulsive interactions, we find that the magnitudes are of the same order as the bonding interactions, if not greater. Thus, one cannot ignore the repulsive interactions when calculating the total energy of the system and doing so is completely baseless. As a result, when we properly calculate all bonding and non-bonding interactions for both structures 1 and 2, we get the immediate realization of the lowest energy state.



1 **1'** **2** **2'**

$$\Psi_{\mathrm{VB}}(\mathbf{1}) = \left|(x_1\bar{x}_1x_2 + x_1\bar{x}_2x_2)(\bar{y}_1y_1\bar{y}_2 + \bar{y}_1y_2\bar{y}_2)\right|$$

$$\Psi_{\mathrm{VB}}(\mathbf{2}) = \left|(x_1\bar{x}_1x_2\bar{x}_2)(y_1\bar{y}_2 - \bar{y}_1y_2)\right|$$

Figure 1: The four possible distributions of six electrons in four atomic pp orbitals of dioxygen, leading to a total spin component $S_z = 0$. (Figure is adopted with permission from reference 11)

Let us now construct the VB wavefunctions for both the structures 1 and 2. The equation (i) shows how to write the VB expression for a 3e bond.

$$\mathrm{A} \therefore \mathrm{B} = \mathrm{A}^{\bullet}\,{:}\mathrm{B} \leftrightarrow \mathrm{A}{:}\,{}^{\bullet}\mathrm{B} \qquad \Psi(\mathrm{A} \therefore \mathrm{B}) = \mathrm{N}'\,(|\,...\mathrm{a}\bar{a}\mathrm{b}| + |\,...\mathrm{a}\bar{b}\mathrm{b}|) \qquad \rightarrow \quad \text{(i)}$$

We can derive the wavefunction for structure 1 from equation (i), which considers these electronic distributions as two independent 3e/two-orbital systems that are orthogonal to each other, and both lie in the π_x and π_y planes. Thus, it will generate the wavefunction Ψ_{VB}**(1)** of Figure 1 with the total S_z spin component set to zero, making this wavefunction suitable for producing both singlet and triplet states. By solving this wavefunction, we can get the energy of the structure 1 as shown in the equation (ii).

$$E(1) = 2\beta(1 - 3S)/(1 - S^2) \qquad \rightarrow \qquad \text{(ii)}$$

Similarly, we can derive the energy of the structure 2 within the VB framework, as shown in equation (iii). Here, the first term represents the 2e bonding energy and the second one describes the 4e repulsion.

$$E(2) = 2\beta S/(1 + S^2) - 4\beta S/(1 - S^2) \quad \rightarrow \quad \text{(iii)}$$

To reach our conclusion, we can simply compare the energy terms generated by both structures. The comparison of both terms, as shown in equation (iv), demonstrates that the diradical type structure 1 has less energy than the doubly bonded Lewis's structure 2.[11]

$$E(2) - E(1) = -2\beta(1 - S)^2/(1 - S^4) > 0 \quad \rightarrow \quad \text{(iv)}$$

Thus, it is clear from the above discussion that the structure 1 is more stable than the structure 2. Hence, we can conclude from above evidence that VB theory can correctly predict the ground state of O_2 molecule that exhibits paramagnetism.

[Note: To simplify our article, we have omitted the effect of mixing of structure 1 with $1'$ and structure 2 with $2'$ in the preceding discussion. However, interested readers may go through the reference 11 for further study.]

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Series

Shanti Swaroop Bhatnagar Awardees in Chemical Science: Amolak Chand Jain; The Eleventh Recipient Series

The Shanti Swaroop 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 Swaroop 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 1969, Dr. Amolak Chand Jain was awarded the prestigiousShanti Swarup Bhatnagar Award for his contributions in the field of chemical sciences. Dr. Jain's research work is related to the chemistry of natural products, the main emphasis being of polyphenols.

Early life:

Amolak Chand Jain was born on 27 December 1928 to Jugal Kishore Jain and Kala Waiti in the Indian capital of Delhi. He graduated in Chemistry in 1948 from the University of Delhi and passed his master's degree from the same university in 1950. He did his doctoral studies under the guidance of T.R. Seshadri, a renowned chemist, to secure his PhD in 1954 from University of Delhi. Moving to Cambridge University in 1956, he secured another PhD in 1958 working at the laboratory of George Wallace Kenner, a Fellow of the Royal Society. He also earned the degree of Doctor of Science in 1967.

Academic Career:

A.C. Jainjoined the department of chemistry in the University of Delhi as a lecturer in 1952, starting the career with it. After he achieved the degree of Doctor of Science in 1967, two years later he was appointed as a professor and head of the department of chemistry at the University of Jammu where he stayed till 1973. Then he moved to Himachal Pradesh University as the head of the chemistry department there. In 1978, he returned to Delhi University where he spent the rest of his career. In between, he had short spells at

Texas Agricultural and Mechanical University(1986), Budapest University and University of Mauritius from 1989-1990 as a visiting professor.

He was a senior scientist of the Indian National Science Academy from 1995 to 2000. He is a life member of the International Academy of Physical Sciences, Indian Chemical Society, Indian Science Congress Association and the Chemical Research Society of India. He was a UGC National Professor 1976 and is and elected fellow of the Indian National Science Academy and the National Academy of Sciences, India.

Research work:

Working on polyphenols early in his research career, Jain elucidated the structure of several compounds in natural products. He worked on the biogenesis of chlorophylls and developed new protocols for the synthesis of polyphenols. Later, he focused on the chemistry of flavonoids and isoflavonoids. He has published his research findings by way of over 275 articles published in peer-reviewed journals. He also authored a text book on organic chemistry.

Awards:

- Shanti Swaroop Bhatnagar Award in 1969

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Photodynamic Therapy (PDT): A Non-Invasive Cancer Treatment Regimen

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Abstract

Photodynamic Therapy (PDT) is a minimally invasive and cost-efficient treatment modality against a range of cancers and non-cancerous diseases. It relies on three basic elements - a photosensitizer (PS), molecular oxygen and light of suitable wavelength. Following PS injection, it is activated by light of the appropriate wavelength, resulting in the generation of highly reactive oxygen species (ROS), which causes photodynamic cytotoxicity. PDT not only decrease malignant cell proliferation, but it also can create an acute inflammatory milieu around the targeted tumors and boost antitumor immunity. Despite its clinical effectiveness, PDT has certain drawbacks; including photosensitivity following treatment, restricted light dosage delivery, and inefficiency in tumour hypoxia conditions. To address all of the concerns that have arisen during treatment, PDT has been coupled with other materials or treatment techniques such as surgery, radiation therapy, chemotherapy, and immunotherapy and so on. This article will provide a brief overview of PDT, including its fundamentals, clinical applications, limits, and current breakthroughs in PDT.

Keywords: photodynamic therapy (PDT), photosensitizer, cancer, tumor, combined modality

1. Introduction:

Photodynamic Therapy (PDT) is a hundred years antique therapy, in which a combo of the non-poisonous photosensitizing drug, molecular oxygen, and harmless visible light of suitable wavelength is applied to the diagnosis and prognosis of oncological and non-oncological disorders.[1–2]

1.1 A Historical Review

Oscar Raab, a medical student working under the guidance of Professor Herman von Tappeiner, discovered in 1990 that acridine could kill paramecium when exposed to light.

He noted that the mortality was caused by the effect of energy transition from light to acridine, which is identical to the photosynthesis process found in plants. Similarly, many types of photosensitizers have been introduced into clinics for the identification of various forms of malignancy. Thus, Photodynamic Therapy (PDT) gradually evolved as a revolutionary, well-studied therapeutic technique for selectively damaging cancer cells (Figure 1) by activating a chemical component with light while leaving unexposed healthy cells unharmed and unaltered.[1, 3–5]

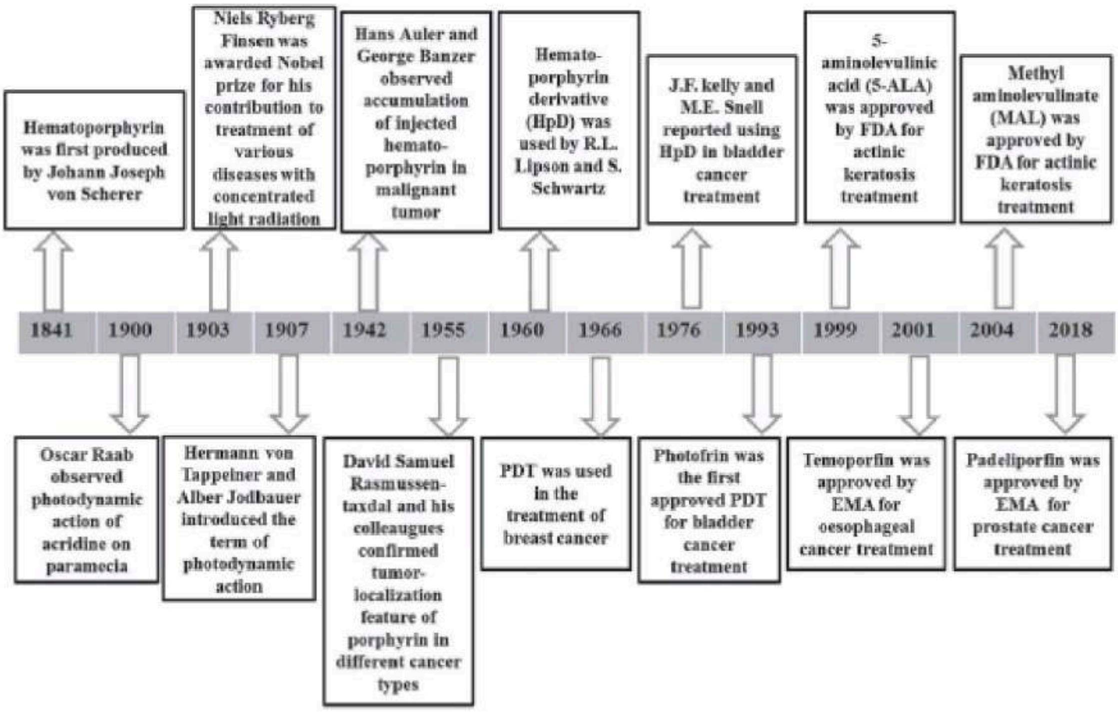


Figure 1: Development of PDT

1.2 Basics of PDT

In PDT, drug molecules are typically activated using low energy visible light with a wavelength between 600 and 850 nm that has the strongest skin penetration power.[3–5] PDT's fundamentally complicated mechanism may be subdivided into two types: type I and type II, with each requiring three non-toxic elements: molecular oxygen, a photosensitizer, and light. Through the production of reactive molecular species, these three fundamental components achieve the desired effects and confer cytotoxicity. This highly reactive ROS can trigger cell death by either apoptosis or necrosis. The first stage in the general process of PDT is the systematic localization of the photosensitizer in target tissue. When the accumulation is finished, it is "switched on" using an appropriate wavelength of light (red light, 600 nm) (Figure 2). PS converts into the excited singlet state after absorbing a photon, and subsequently into the excited triplet state via intersystem crossover.[6–8]

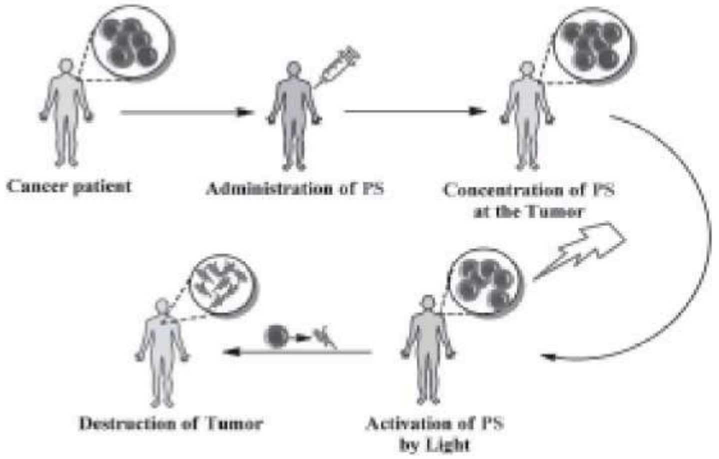


Figure 2: Clinical application of PDT

Later, the long-lived excited triplet state encourages the formation of ROS by undergoing two types of chemical interactions. In Type-I process, photosensitizer reacts directly with cell membrane/a molecule leading to the generation of hydroxyl radical (OH•), hydrogen peroxide (H_2O_2) and superoxide anion radical ($O_2^{\bullet-}$). In Type-II mechanism of PDT, the photosensitizer transfers its electronic energy directly to oxygen ($PS \rightarrow O_2$), leading to the formation of highly reactive oxygen species i.e. singlet oxygen ($^1\Delta g$) (Figure 3). Some studies that may be done to separate the two mechanistic paths include the lifespan experiment, azide anion quenching of singlet oxygen, spin-trapping of hydroxyl radical and superoxide radical and so on.[9–11]

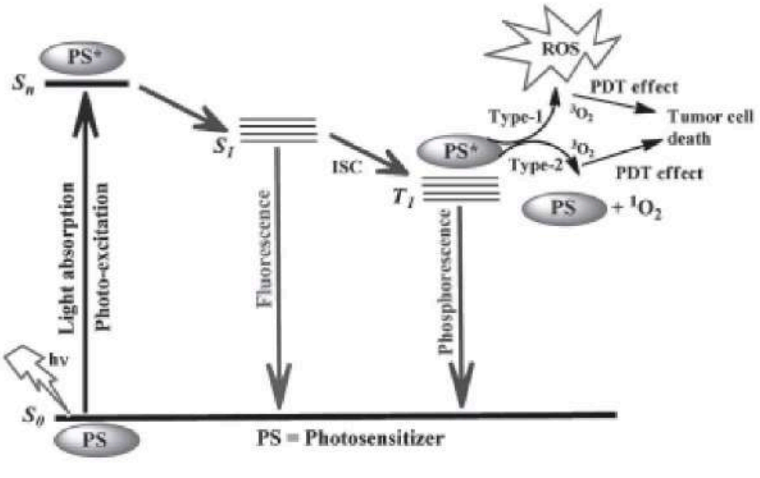


Figure 3: Jablonski diagram indicating the photo processes involved in PDT

1.3 Ideal photosensitizer for PDT

A good photosensitizer should be a single agent made under good manufacturing practice, managed according to quality standards, and produced at a cheap cost. They should have excellent stability, low dark toxicity, a large molar absorptivity coefficient in the PDT window range, quick systematic clearance, a long lifespan, and improved water solubility. A good PS should be extremely tumor specific and chemically pure. When exposed to light, they should exhibit large quantum yields (triggers the generation of ROS in good amount). Unsurprisingly, there is no (ideal) photosensitizer for PDT because no one can meet all of the above criteria.[5, 12]

1.4 Well-known photosensitizers in PDT

Photofrin was the first certified photosensitizer in Canada in 1993, invented by Thomas Dougherty for the treatment of bladder cancer.[3] Because of its many limitations, such as unclear composition, low molar absorption coefficient at 630 nm, extended skin sensitivity, hepatotoxicity etc., the use of Photofrin (Figure 4) for PDT has been restricted, prompting the design and synthesis of next generation photosensitizers. Other FDA-approved photosensitizing medicines include verteporfin (Visudyne), temoporfin (Foscan), and talaporfin (Laserphyrin) (Figure 4).[1]

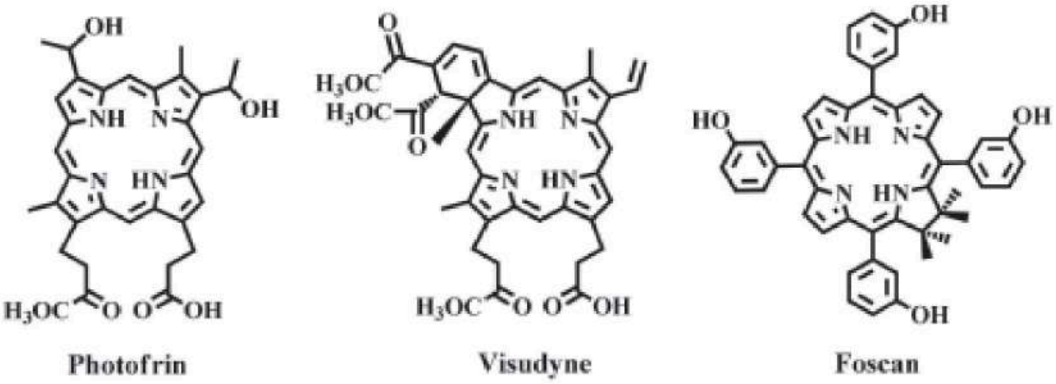
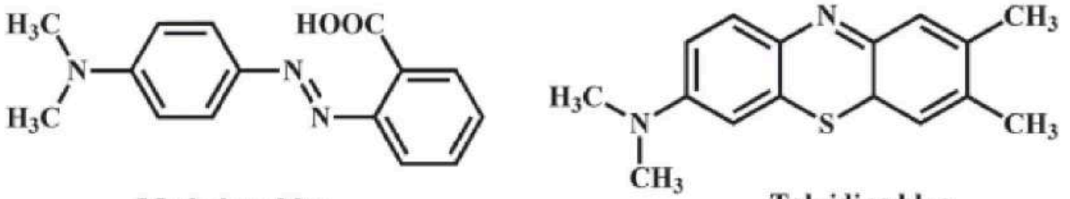


Figure 4: Some FDA approved well-known photosensitizers (porphyrinic)

Photosensitizers are divided into two types: porphyrins and non-porphyrins. Porphyrinic photosensitizers are further classified as first, second, and third generation photosensitizers. A first generation photosensitizer is hematoporphyrin derivative (HpD), which is a combination of monomeric, dimeric, and oligomeric species produced from hematoporphyrin.[12] Due to several limitations associated with first generation photosensitizers, their application in clinical trials has been limited, and several second generation photosensitizers have been created as a result. Although the second generation photosensitizers function better than the first, they produce skin toxicity owing to the absorption of longer wavelength light. Benzoporphyrins, purpurins, texaphyrins, phthalocyanins, naphthalocyanins, protoporphyrins, and others are examples. Third generation photosensitizers are second generation photosensitizers that bind to antibodies and liposomes for selective accumulation within tumour tissue. Nonporphyrinic photosensitizer development has trailed much behind that of porphyrin-based PDT. Until now, cationic photosensitizers such as chalcogenopyrylium dyes, phenothiazinium and benzo[a]phenothiazinium derivatives such as methylene blue and toluidine blue (Figure 5) have received the majority of attention. While there are a number of "other" nonporphyrin photosensitizers (178), there has been remarkably little progress in developing these compounds as photosensitizers in recent years. Further research into these mostly undiscovered groups of chemicals, which include psoralens, anthracyclines, triarylmethanes, and acridines, is undoubtedly necessary. [12–14]



Methylene blue **Toluidine blue**

Figure 5: Two examples of non porphyrinic photosensitizers

2. Mechanism of cell death induced by PDT

Cell death is a vital biological process that occurs when defective or damaged cells are eliminated, making it important phenomena for organogeny and tissue maintenance. This is divided into two categories: apoptotic and nonapoptotic (which covers autophagy and necrosis). PDT-generated ROS initiate a series of metabolic reactions that can result in these three types of cell death pathways. The primary mechanisms in the cytotoxic effects of PDT are apoptosis and necrosis. PDT induces apoptosis via oxidative stress when the photosensitizer is in the cell membrane or other cell organelles such as the nucleus, mitochondria, endoplasmic reticulum etc. The kinetics of the two methods are mostly determined by the biochemical features of the photosensitizer, the total light dosage of PDT drug utilised, the exposure settings, and the kind of cells used. Several *in vitro* and *in vivo* studies have shown that malignant cells can be immediately destroyed through apoptosis and necrosis.[15–17]

3. Conclusion

Despite being discovered many years ago, PDT is still in its infancy. Due to drawbacks, such as post-treatment photosensitivity, treatment efficacy being dependent on accurate light delivery to the tumour, tissue oxygenation being critical to the photodynamic effect, and being impossible to treat metastatic cancers with current technology, only a few compounds have gained access to clinics. Much more research in this field is needed to bring this modality to mainstream cancer treatment regimens.[18–19] A viable therapeutic technique nowadays is combination therapy, which has gained general acceptance as an effective method of cancer treatment. Because PDT gives cytotoxic benefits through an unusual action mechanism, it can be used safely alongside other therapy methods that do not cause cross-resistance. As a result, PDT can be employed in conjunction with a wide range of treatment modalities, including surgery, radiation therapy, chemotherapy, immunotherapy, and so on. According to literature reports, PDT can totally cure animals with big tumours when paired with immunotherapy and chemotherapy.[20] Based on the genetic sequencing of the patient's cancer cells, medications can be used to inhibit the downstream pathways that govern tumour growth, allowing for the development of a tailored anticancer treatment that is both effective and efficient. Furthermore, low-dose radiation treatment aids in the breakdown of immunological tolerance in cancer patients and the development of powerful anticancer immune responses. Thus, if combination therapy is used correctly, treatment for many forms of cancer will become simple, and cure will become a reality.[21]

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Role of Supercapacitors as a new energy storage device

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Abstract

Electrochemical capacitors, also known as supercapacitors can store energy using either ion adsorption (electrochemical double layer capacitors) or fast surface redox reactions or faradaic reactions (pseudo-capacitors/redox-capacitors). They can complement or replace batteries in electrical energy storage and harvesting applications, when high power delivery or uptake is needed. A noteworthy advance in performance has been accomplished through recent advances in understanding charge storage mechanisms and the development of advanced nanostructured materials. This review article describes the current progression of supercapacitors as energy storage device.

■ Introduction

The viable generation of renewable energy such as solar and wind energy depends on a number of natural conditions such as duration of the day or night, velocity and direction of wind. However, supply of such renewable energies are non-continuous. Therefore, high performance energy storage devices are essential to store this produced energy and to stabilize the connected electricity grid. Current research and development on electrochemical power sources are mainly focused on fuel cells, batteries and electrochemical capacitors (EC) and are directed towards obtaining high specific energy, high specific power, long cycle life, etc., at relatively low cost.[1,2] The supercapacitors, also known as ultracapacitor or electrochemical capacitor, differs from a regular capacitor in that it has a very high capacitance. A capacitor stores energy by means of a static charge. Applying a voltage difference on the positive and negative plates charges the capacitor. Farad (F) is the unit of capacitance, which corresponds to the storage of one coulomb (C) of electric charge by applying 1 volt of voltage. Capacitors can be classified into three types and the most basic is the electrostatic capacitor with a dry separator. This capacitor has a very low capacitance in the order of a few pico-farad (pF) to low micro-farad (μF) and can be used to filter signals and tune radiofrequencies. The next type is the electrolytic capacitor having capacitance in the order of high micro-farad (µF) and can be used for power filtering, buffering as well as coupling. The third type is the supercapacitors or electrochemical capacitors or ultracapacitors. It has very capacitance in the order of farad (F). The supercapacitor is ideal for energy storage which undergoes frequent charge-discharge cycles at high current and short duration. Due to their high specific power, supercapacitors have multiple applications including automobiles, hybrid electric vehicles and various electric vehicles (for acceleration and for recuperation of brake energy).3,4 While a battery is a high energy and low power device, extensively used in conventional applications, the supercapacitor acts as a low energy and high power device and is ideal for use in high power pulse necessities.[5,6] Unlike a battery, supercapacitors possess a high power density and longer cycle-life. They fill the gap between batteries and conventional dielectric capacitors as can be observed in Ragone plot,[1,3] which is the plot of power density against energy density. They also cover a wide range of specific energy density from 0.05 to 15 Whkg^{-1} and a specific power density from 10 to 106 Wkg^{-1}.[3] Figure 1 shows a typical Ragone plot, which indicates that the supercapacitors lie between traditional capacitors and batteries in terms of both energy density and power density. Table 1 illustrates the properties of different energy storage devices. The very large capacitance of these devices arises from the double layer charging processes at the electrode|electrolyte interfaces. Alternatively, a fast reversible faradaic reaction occurring at or near the electrode surface can also contribute to the overall capacitance, which is known as pseudocapacitance. In addition to these, a new type of EC known as hybrid ultracapacitor has been developed recently, which can provide energy densities of batteries and power densities of capacitors. Hybrid ultracapacitors consist of a rechargeable battery-electrode and an electrical-double layer electrode. In literature, three different kinds of supercapacitors based on carbon-carbon,[7,8] transition metal oxides[9,10] and conducting polymers[11–13] have been reported. This review article focuses on the principle, classification and performance of supercapacitors along with the current research development on various electrode materials for supercapacitor applications.

■ Historical background of supercapacitor with its development

The first patent based on the concept of EC was filed by Becker in 1957.[14] They used high specific surface area (SSA) carbon coated on a metal current collector in a sulphuric acid solution. In 1971, NEC(Japan) developed aqueous electrolyte capacitors under the energy company SOHIO's license for power saving units in electronics.[14] In 1978, this technology as "supercapacitors" was marketed for computer memory backup. This application can be considered as the starting point for the use of electrochemical capacitors in commercial device. It was not until the 1990s that the advancement in material science and manufacturing methods led to the improvement of performance and reduction of cost for ECs. New applications in mobile electronics, transportation, renewable energy production, memory back-up systems, industrial power/energy management and aerospace systems bolstered further research and development. A more recent application of supercapacitors in Airbus A380 planes has shown the safer and reliable performance of supercapacitors for large scale implementation. Most of the commercially available supercapacitor products have a specific energy density less than 10 Whkg^{-1}, which is 3 to 15 times lower than batteries (150 Whkg^{-1} for lithium ion batteries). Since the introduction of lithium (Li) ion batteries in 1990 by Sony, great efforts have been taken to improve its performance and reduce its cost.[15] Because Li ion batteries suffer from somewhat slow power delivery or uptake, faster and higher power energy storage devices are required in various applications. Table 2 illustrates the comparison between the supercapacitor and a typical Li-ion battery. This limitation of Li-ion battery led to the development of power devices such as supercapacitors, which can be fully charged or discharged in seconds. As a consequence, supercapacitors can provide an important role in complementing or replacing batteries in the energy storage field, such as uninterruptible power supplies and load-levelling. There has been great deal of research effort on increasing the energy performance of supercapacitors to be close to or even beyond that of batteries.

■ Principle and performance of Supercapacitors

A supercapacitor supplies energy employing either ion adsorption (electrical double layer capacitors, EDLCs) or by fast and reversible faradaic reactions (pseudocapacitors). These two mechanisms can work concurrently, depending on the nature of electrode material.

3.1 Mechanism of double-layer capacitance

EDLCs are electrochemical capacitors which can store the charge electrostatically using reversible adsorption of ions of the electrolyte onto active materials that are electrochemically stable and have high accessible specific surface area. Charge separation occurs due to the polarization at the electrode | electrolyte interface, producing a double layer, whose capacitance C is described as

$$C = \frac{\varepsilon_r \varepsilon_0 A}{d} \quad \text{or} \quad C/A = \frac{\varepsilon_r \varepsilon_0}{d} \qquad (1)$$

Where ε_r is the electrolyte dielectric constant, ε_o is the dielectric constant of the vacuum, d is the effective thickness of the double layer (distance of charge separation), and A is the surface area of the electrode. This model of double layer capacitor for electrode | electrolyte interface was introduced by Helmholtz in 1853. Figure 2 shows the Helmholtz double layer model at the electrode | electrolyte interface. This capacitance model was later modified by Gouy and Chapman, and Stern and Geary, who suggested the presence of a diffuse layer in the electrolyte due to the accumulation of ions close to the electrode surface.[16] The double layer capacitance value is between 5 to 30 µF cm^{-2} depending on the electrolyte used. Higher capacitance values can be obtained in aqueous alkaline or acidic solution compared to organic electrolytic solutions. Organic electrolytic solutions are widely used for obtaining a much higher operation voltage. The maximum energy stored and power delivered for a single cell supercapacitor are given by eqns (2) and (3), respectively.

$$E = \frac{1}{2} C_T V^2 \qquad (2)$$

$$P = \frac{V^2}{4R_s} \qquad (3)$$

Where V is the cell voltage in volts, C_T is the total capacitance of the cell in farads, R_s is the equivalent series resistance (ESR). Hence, a high performance supercapacitor must simultaneously satisfy the requirements of large capacitance value, high operating cell voltage and minimum ESR. It is obvious that the development of both electrode material and electrolyte solution are essential to optimize the overall performance of the supercapacitor. Figure 3 shows the schematic diagram of a two cell supercapacitor device made of porous electrode along with the electrical double layer structure based at a positively charged electrode surface. There is no faradaic (redox) reaction at the EDLC electrodes due to electrostatic charge storage mechanism. A supercapacitor electrode must be considered as a blocking electrode from an electrochemical point of view. The major difference from batteries is that there is no limitation by the electrochemical kinetics through a polarization resistance (low ESR values). In addition to this, the surface storage mechanism allows very fast energy uptake and delivery and better power performance. The absence of faradaic reaction eliminates the swelling in the active materials during charge/discharge cycles. Since, $C \propto A$, increasing the specific surface area (SSA) of the electrode material used in supercapacitors can provide large capacitance values. For examples, porous activated carbon has much large SSA (1000-2000 m^2g^{-1}) which can store 100-1000 times more charge (10-1000 F g^{-1}) than the conventional capacitor.

3.2 High surface area Active Materials

The main factor to obtain high capacitance value by charging the double layer is in using high SSA blocking and electronically conducting electrodes. Graphitic carbon satisfies all the requirements for supercapacitor applications such as high conductivity, electrochemical stability and open porosity. Activated, templated and carbide derived carbons, carbon fabrics, fibers, nanotubes and nanohorns have been tested for EDLC applications. Activated carbons (ACs) are the most widely used electrode materials owing to their high SSA, low price and easy workability.[17–19] ACs are derived from carbon-rich organic precursors by carbonization (heat treatment) in an inert atmosphere followed by selective oxidation in carbon dioxide (CO_2), water vapour or potassium hydroxide (KOH) to increase the SSA and pore volume. Natural materials, such as coconut shells, wood, pitch, coal or synthetic materials like polymers can be used as precursors. However, AC based supercapacitors have limited energy storage capacity (typically below 200 F g^{-1}) and lower cell voltage in aqueous electrolyte due to the limitation of potential window as a consequence of water decomposition. The best carbon electrodes have surfaces as high as 3000 m^2 per gram of material. The electrode capacitance increases linearly with the carbon surface area and may reach a capacitance of 250 F g^{-1}. They are usually prepared from high surface area carbon powders or fibers. Activated carbons such as activated carbon powder (ACP), activated carbon fiber cloth (ACF-cloth), and synthetic carbon aerogel have been investigated for EDLC applications. Figure 4 shows the typical cyclic voltammogram of a two-electrode EDLC cell based on AC powders coated on aluminum foil along with the picture of a commercial EDLC. The typical rectangular shape cyclic voltammogram is a characteristic of a pure double layer capacitance mechanism for charge storage according to eq (4).

$$I = C \times dV/dt \qquad (4)$$

Where I is the charging current, (dV/dt) is the potential scan rate and C is the double layer capacitance. Table 3 summarizes some properties and characteristics of various carbon electrode materials for supercapacitors. Graphene based materials, including zero-dimensional fullerenes, one dimensional carbon nanotubes (CNTs), two dimensional graphene and three dimensional graphite are of particular interest due to their exceptional electrical and mechanical properties and unique structures.[20] Graphene, a two dimensional flat monolayer of sp^2 hybridized carbon bonded in a hexagonal lattice is the mother of all the graphitic carbon.[21,22] Recent researches on electrode materials have been mainly focused on the carbon nanostructures like carbon nanotubes (CNTs). CNTs with excellent electrical conductivity and high surface areas have been fabricated for supercapacitors since late 90's.[23,24] However, CNT-based supercapacitors have not met the expected performance due to the observed contact resistance between the electrode and current collector [25,26] and also due to the high cost. Hence, many studies have been carried out to improve the performance of CNT-based supercapacitors by growing CNTs directly on bulk metals to remove the contact resistance.[27] Recently, graphene based electrode material has been used for supercapacitor applications[28] and two graphene supercapacitor application studies had been reported with the specific capacitance of 117 F g^{-1} in aqueous H_2SO_4[29] and 135 F g^{-1} in aqueous electrolyte30 based on a multilayered graphene material. In contrast to the conventional high surface materials, the effective surface area of graphene based materials as capacitor electrode materials does not depend on the distribution of pores at the solid state,[30] which is different from the current supercapacitors fabricated with activated carbons and carbon nanotube. Obviously, the effective surface area of graphene materials should depend highly on the layers. Therefore, the single or few layered graphene should be expected to exhibit higher effective surface area and thus better supercapacitor performance.

3.3 Redox-based Electrochemical Capacitors

Some ECs use fast, reversible redox reactions between the electrolyte and some electro-active species at the surface of active materials. The most commonly known active materials are transition metal oxides such as ruthenium oxide (RuO_2)[31] iridium oxide (IrO_2), manganese dioxide (MnO_2)[32,33] Fe_3O_4 as well as electrically conducting polymers[34,35] and surface functional groups on carbon.[36] Different from the EDLCs, pseudocapacitance arises for thermodynamic reasons between the extent of charge acceptance (Δq) and the change of potential (ΔV). The derivative $C = d(\Delta q)/d(\Delta V)$ corresponds to a capacitance referred to as the pseudo-capacitance. While the pseudocapacitance can be higher than EDL capacitance, it suffers from the drawbacks of low power density and lack of stability during cycling. RuO_2 is widely studied because it is conductive and has three distinct oxidation states accessible within 1.2 V. The pesudocapacitive behavior of RuO_2 in acidic solutions has been known in the past 30 years.[1] It can be described as a fast reversible electron transfer together with an electro-adsorption of protons on the surface of RuO_2 particles as shown in eq (5) where Ru oxidation states can change from (II) to (IV).

$$RuO_2 + xH^+ + xe^- \leftrightarrow RuO_{2-x}(OH)_x \qquad (5)$$

Where $0 < x < 2$. The continuous change of x during proton insertion or de-insertion occurs over a window of ~ 1.2 V and leads to a capacitive behavior with ion adsorption following Frumkin type isotherm. Although, specific capacitance of more than 600 F g^{-1} has been reported, but the high cost and I-V voltage window limits the applications of RuO_2 based aqueous electrochemical capacitors for large scale commercial use. Less expensive oxides of iron, vanadium, nickel and cobalt have been tested in aqueous electrolytes,[37] but none has been investigated as much as MnO_2. MnO_2 is one of the most studied materials as a low cost alternative to RuO_2. The charge storage mechanism is based on surface adsorption of electrolyte cations C^+ (K^+, Na^+) as well as proton incorporation according to the reaction shown by eq (6).

$$MnO_2 + xC^+ + yH^+ + (x+y)e^- \leftrightarrow MnOOC_xH_y \qquad (6)$$

Many types of conducting polymers (polyaniline, polypyrrole, polythiophene and their derivatives) have been tested as pseudo-capacitive materials in EC.[38] Polyaniline (PANI) is one of the most important organic conducting polymers. Its unique advantages include easy preparation in aqueous medium, good environmental stability in air, improved electronic properties, electrochromic effects, good electrochemistry, and moderately high conductivity in the doped form. All these have made it an exceptionally versatile material with application in such areas as batteries, electronics, nonlinear optics, sensors. In addition to this, PANI is also one of the attractive electrode materials used in supercapacitors due to the advantageous properties including low cost compared to noble metal oxides and high doping-dedoping rate during charge-discharge process. However, conducting polymers such as PANI have lower cyclic life than carbon-based electrodes due to the poor stability of the redox sites in the polymer for many repeated redox processes. Although, porous carbon materials like activated carbon and PANI are widely used as electrode materials in supercapacitors, the use of these individual materials in supercapacitors is limited due their drawbacks. However, if the advantages of porous carbon materials are combined with PANI, the resulting composites will provide synergistic performance as electrode materials. Therefore, it is necessary to fabricate a feasible composite electrode by combining PANI with activated carbon for applications in supercapacitors.

3.4 Hybrid Supercapacitors

Hybrid systems can be alternative to conventional pseudocapacitors or EDLCs by combination of a battery like electrode (energy source) with a capacitor like electrode (power source) in the same cell. An appropriate electrode combination can even enhance the cell voltage with improvement in both power and energy densities. The hybrid concept originated from the Li-ion battery field, when Amatucci's group combined a nanostructured lithium titanate anode ($Li_4Ti_5O_{12}$) with an activated carbon positive electrode in 1999.[39] They fabricated a 2.8 V system for the first time with specific energy density exceeding 10 $Whkg^{-1}$. The titanate electrode can provide high power capacity and no solid interphase formation. Following this pioneering work, many studies have been carried out on various combinations of a lithium-insertion electrode with a capacitive carbon electrode. Fuji Heavy Industry developed the Li-ion capacitor using a pre-lithiated high SSA carbon anode together with an AC cathode.[40,41] Currently, two different approaches have been carried out to fabricate hybrid ultracapacitors: (i) pseudo-capacitive metal oxides with a capacitive carbon electrode, and (ii) Li-insertion electrode with a capacitive carbon electrode. Various combinations of positive and negative electrodes have been tested in the past. But, in most of the cases, the pseudo-capacitive electrode led to an increase in the energy density at the cost of cyclability. This is certainly the major drawback of hybrid devices. A combination of a carbon electrode with a PbO_2 battery like electrode using H_2SO_4 solution can work at 2.1 V offering a low-cost device for cost-sensitive applications.[42] Table 4 summarizes the various hybrid ultracapacitors.[43] The possible applications of hybrid ultracapacitors are in rural lighting, energy storage, energy management, energy efficiency and power conversion.

■ Applications of Electrochemical Capacitors

Small size supercapacitors are widely used as maintenance free power sources for IC memories and microcomputers. Among newly proposed applications for large size supercapacitors are load levelling in electric and hybrid vehicles, telecommunication and power quality and reliability requirement in uninterruptible power supply (UPS) installations. In general, supercapacitors can be classified into two application domains. The first one corresponds to the high power applications, where the batteries have no representative access. The EDLCs, thanks to their high power capability, will allow new opportunities for power electronics. All applications where short time power peaks are required can be provided by these capacitors. Typical examples where a big current is required during a short time are the fast energy management in hybrid vehicles or the starting of heavy diesel engines. The second one corresponds to the low power applications, where the batteries could be more suitable but are at the origin of maintenance problems or of insufficient lifetime performance. The supercapacitors, even if they are much bigger, bring enough advantages to substitute the batteries. In this field, the UPS as well as security installations are the most representative examples.

■ Summary and Outlook

This review article illustrates an updated version of the recent development on the supercapacitors. Supercapacitors may be used wherever high power delivery or electrical energy storage is required. Therefore, numerous applications including automobiles, hybrid electric vehicles and various electric vehicles are possible. The use of supercapacitors allows a complementation of normal batteries. In combination with batteries the supercapacitors improve the maximum instantaneous output power as well as the battery lifetime. In order to increase the voltage across a supercapacitor device, a series connection is needed. Future generations of ECs are expected to come close to the current Li-ion batteries in energy density with maintaining their power density.

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Table 1

Comparison of properties of some energy storage devices

Property	Conventional capacitor	EDLC	Battery
Energy density ($Whkg^{-1}$)	0.1	3	100
Power density (Wkg^{-1})	10^7	3000	100
Time of charge (s)	10^{-3}-10^{-6}	0.3-30	> 1000
Time of discharge (s)	10^{-3}-10^{-6}	0.3-30	1000-10,000
Cyclability	10^{10}	10^6	1000
Typical lifetime (years)	30	30	5
Efficiency (%)	>95	85-98	70-85

Table 2

Comparison between the supercapacitor and a typical Li-ion battery

Function	Supercapacitor	Lithium-ion battery
Charge time	1-10 seconds	10-60 minutes
Cycle life	10^6	500
Cell voltage	2.3 to 2.75 V	3.6 to 3.7 V
Specific energy ($Whkg^{-1}$)	5	100-200
Specific power (Wkg^{-1})	Up to 10,000	1000 to 3000
Cost per Wh	\$20	\$2
Service life (in vehicle)	10 to 15 years	5 to 10 years

Table 3

A comparison of various carbon electrode materials for supercapacitors

Carbon based material	**Specific surface area (m^2 g^{-1})**	**Density (g cm^{-3})**	**Electrical conductivity (S cm^{-1})**	**Cost**	**Specific capacitance (F g^{-1})**	
					Aqueous electrolyte	**Organic Electrolyte**
Fullerene	1100-1400	1.72	10^{-8}-10^{-1418}	Medium	-	-
CNTs	120-500	0.6	10^{4}-10^{519}	High	50-100	< 60
Graphene	2630	> 1	10^{6}	High	100-200	80-110
Graphite	10	2.26	10^{423}	Low		
Activated carbon	1000-3500	0.4-0.7	0.1-1	Low	< 200	< 100
Templated porous carbon	500-3000	0.5-1	0.3-10	High	120-350	60-140
Activated carbon fibers	1000-3000	0.3-0.8	5-10	Medium	120-370	80-200
Carbon aerogels	400-1000	0.5-0.7	1-10	Low	100-125	< 80

Table 4

A comparison of various hybrid ultracapacitors

Type of hybrid ultracapacitor	**Voltage (V)**	**Specific capacitance (F g^{-1})**	**Spcific energy density (Whkg^{-1})**	**Specific power density (Wkg^{-1})**
$PbSO_4/PbO_2$- AC	2.25-1.0	-	15.7	8.9
$PbSO_4/PbO_2$- AC	2.3-1.0	-	39.5	-
$Ni(OH)_2$- carbon	1.6-0.6	-	13.9	4.0
NiO-carbon	1.3	38	-	-
$Ni(OH)_2$-CNT	1.6-0	311	25.8	2.8
NiO-AC	1.6-0	73.4	26.1	-
Carbon-Fe_3O_4	1.2-0	37.9	-	-
$Li_4Ti_5O_{12}$- carbon	2.8-1.6	-	13.8	3.8
MnO_2-carbon	2.0-0	21	10.0	16.0

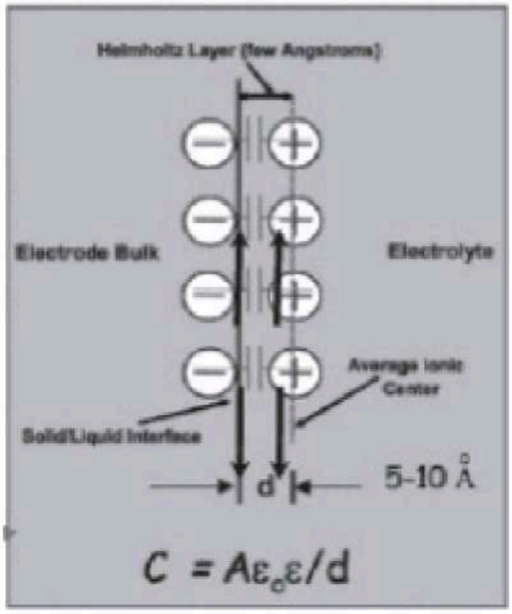
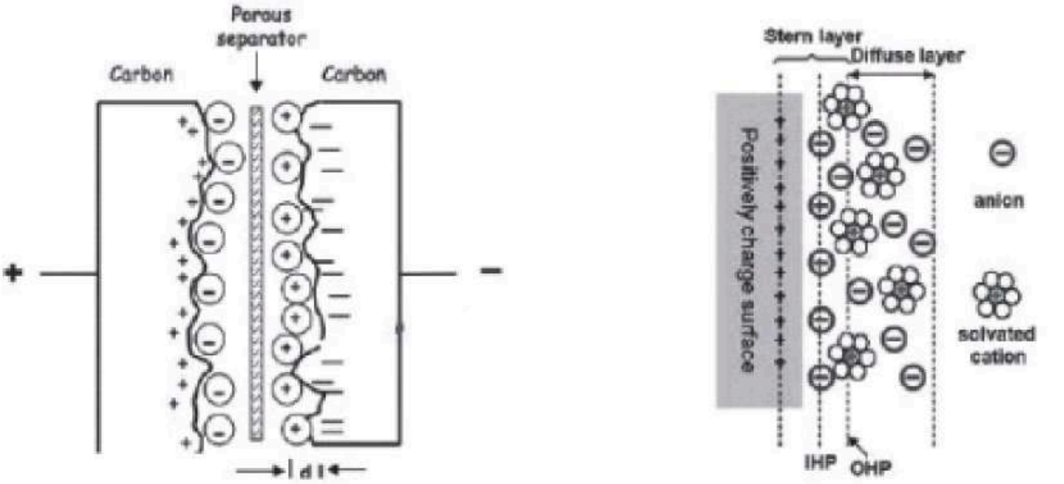


Figure 1. A typical Ragone plot.



$$C \propto \frac{A}{d}$$

A = 1,000 or more m^2/g
d = Angstroms

Figure 2. Schematic diagram showing Helmholtz double layer model at the electrode?electrolyte interface.

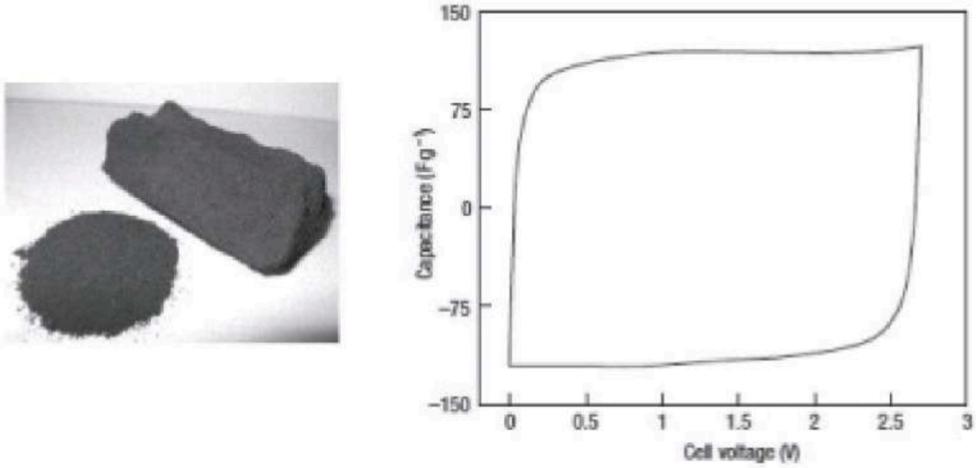


Figure 3. Schematic diagram of a two cell supercapacitor device made of porous electrode along with the electrical double layer structure based at a positively charged electrode surface.

Figure 4. A typical cyclic voltammogram of a two-electrode EDLC cell based on AC powders coated on aluminum foil along with the picture of a commercial EDLC. Assembled supercapacitor device weighing 500 g and rated for 2,600 F. (Photo courtesy of Batscap, Groupe Bolloré, France.)

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■ ■ ■

Sequence Defined Peptoid Polymers for Designing Hierarchical Nanostructures

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1. Introduction

N-substituted glycine oligomers[1], commonly known as peptoids have emerged as an important class of peptidomimetics for designing of new therapeutic[2] and biomaterials[3]. Peptoidsare structurally similar to natural peptides, however unlike natural peptidestheir side chains are present in the nitrogen atoms rather than the α-carbon atoms (Figure 1a). These types of oligomers were initially synthesizedinbiotech/pharma industry to find new candidate for potential drugs by using conventional in solution synthesis methods[4]. In 1992, Zuckermann and coworkers introduced submonomerbased methods to synthesis peptoids in which (Figure 2) synthesis was carried out over a solid resin support, technicallysimilar tostandard Solid Phase Peptide Synthesis (SPPS) method[5]. The submonomer method basically consisted of two repetitive

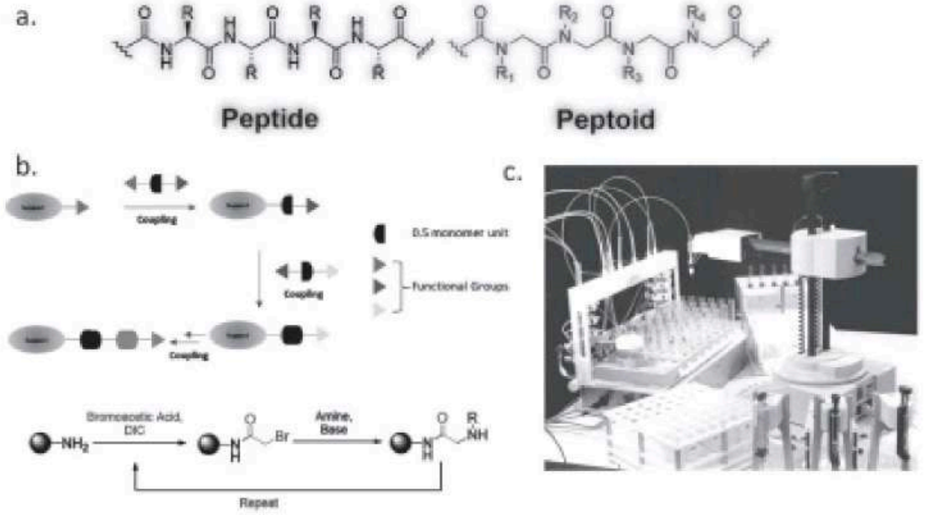

Figure 1: a. Chemical structures of peptide and peptoid. b. submonomer synthetic scheme of peptoid. c. picture of an automated peptoid synthesizer[4]

steps - first, coupling of a haloacetic acid with resin active site and secondly, the displacement of the halogen with suitable amine. These two steps are repeated as required to design sequence defined peptoid polymers (Figure 1b). The development of this easy and modular synthetic method accelerated the peptoid based researches in mid 1990s to design new therapeutic agents. In current days, library of peptoid structures can be generated within a short span of time by means of submonomer synthesis in automated synthesizer. (Figure 1c).

The N-substitution provides several drugs like properties to peptoid such as better cell permeability[6,7] and proteolytic stability[8] than its peptide counterpart. However,such drug candidate tested earlierin mid 1990s were not found to be useful enough for broad applications. One significant restraint of peptoids that limited its broad application was the conformations floppiness of peptoid thatarises due to the lack of H-bond donor, backbone chirality and facile cis-trans isomerization of the tertiary amide bond[9]. Therefore, significant entropic losswere noticed during the drug-target binding event in peptoid based drug screening.[10]

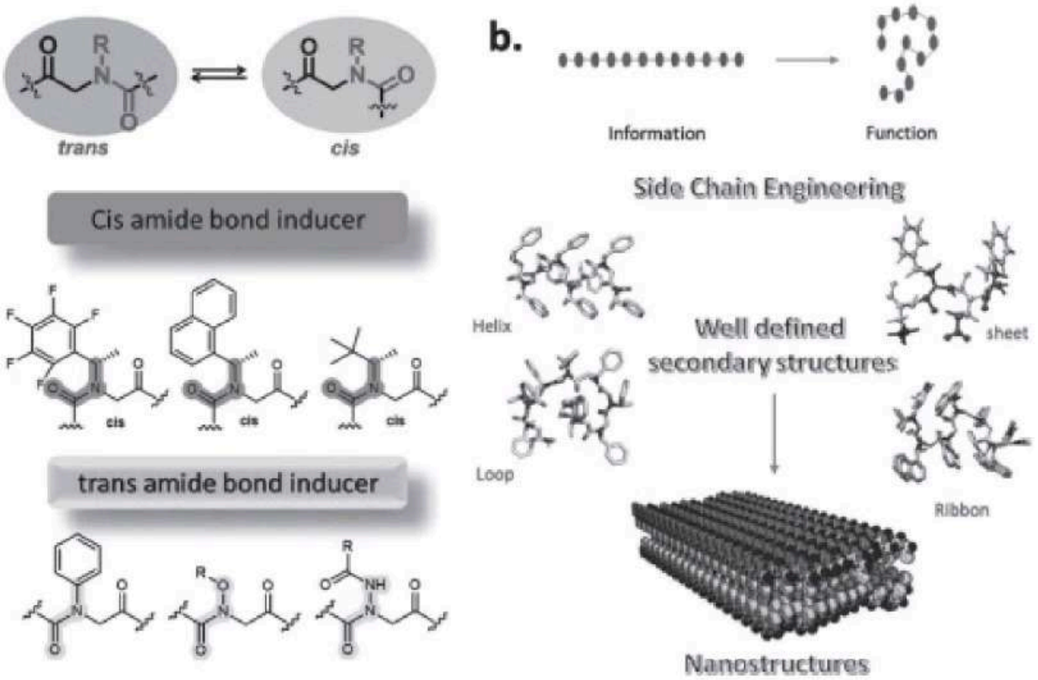

Figure 2: a. cis trans isomerization of peptoid and some cis/trans inducing side chain b. schematic representation of side chain engineering methodology of peptoid to design stable secondary structures.

However, recent development in peptoid structural chemistry researches show that suitable modifications of the side chain can impart required structural stability to peptoids[11,12]. For example, it has been observed that N_{α}-chiral side chain such as 1-

pentafluorophenylethyl[13], 1-naphthylethyl[14], 1-tert-butylethyl[15] can induce cis amide bond geometry and can form stable and robust Polyproline I type of homogenous peptoid polymer. On the other that, side chain with aromatic ring or a heteroatom in the α-position such as N-phenyl[16], N-hydroxy[17], N-alkoxy[18], acyl hydrazide[19] can stabilize trans amide bonds (Figure 2a). Therefore, suitable engineering of the side chain can lead to precise control over the secondary structures of peptoid polymer. In other words, information can be put in the primary sequence of peptoid to generated function via higher ordered structure. In this direction, researchers has so far developed various stable peptoid secondary structure such as helix[14,15], loop[20], sheet[21] and ribbon[22] using sequence defined peptoid polymer. Emergence of this side chain tuning chemistry eventually led peptoid based research towards various other directions as well apart from therapeutic design.

2. Peptoid Based Nanostructures

Due to the precise sequence controllability, robustness and large diversity; peptoids provide unique advantage as programable building blocks for designing hierarchical biomimetic materials[23]. The self-assembly of sequence defined peptoid polymer can easily be controlled by tuning its side chain chemistry to involve in peptoid-peptoid and peptoid-surface interactions. It is known that; hydrophobic interaction plays crucial role in self-assembly process of biomacromolecules. Similarly, inspired from biological self-assembly, researchers have extensively exploited the rolehydrophobic side chains

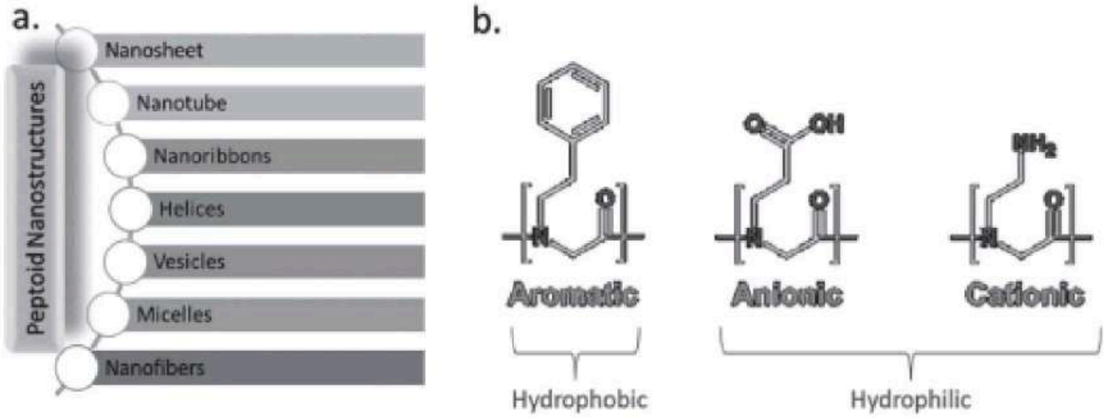

Figure 3: a. Different types of peptoid nanostructures. b. Some commonly used hydrophobic and hydrophilic side chains for designing peptoid nanostructures.

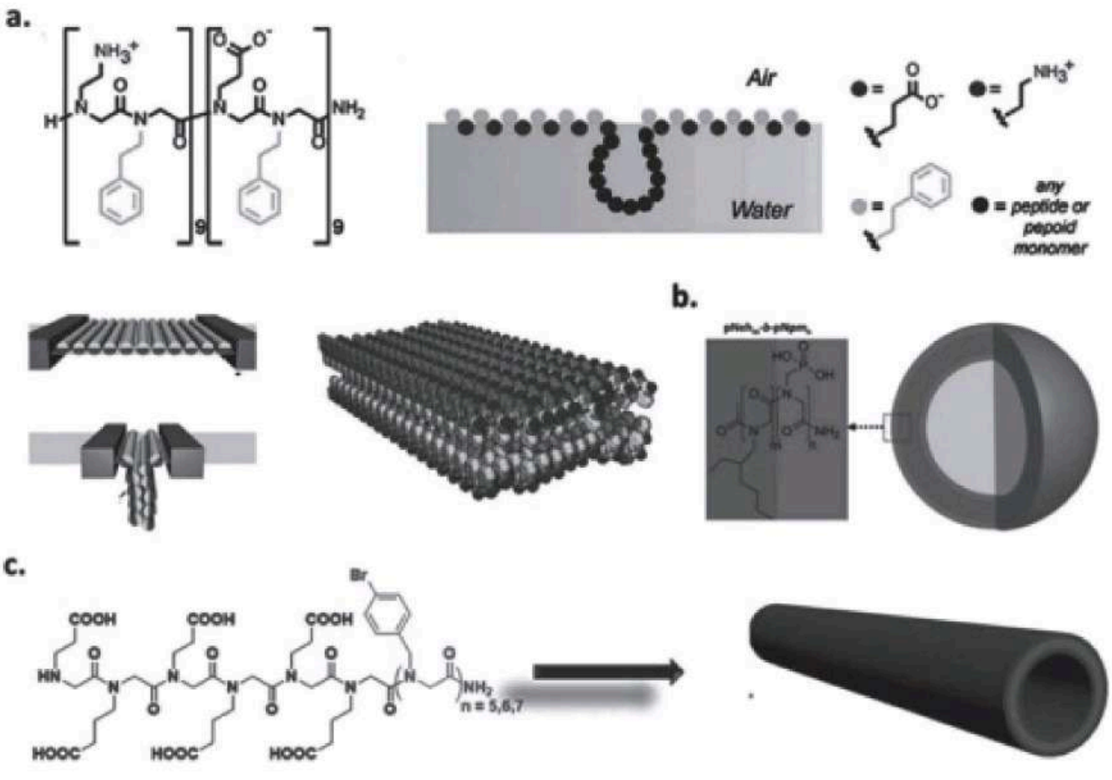

Figure 4: Chemical structure and schematic representation of a. nanosheet forming peptoid. b. vesicle forming peptoid c. nanotube forming peptoid

(Aromatic residues) in forming well defined peptoid self-assembly. Along with, hydrophilic side chains (cationic or anionic) have also been exploited to design peptoid self-assembly as hydrophilic region can provide extra stability to the assembly by maximizing its contact with surface (Figure 3b). Amphiphilic peptoids with both hydrophilic and hydrophobic residues are the among the mostly studied peptoids for designing peptoidassemblies. Some important class of peptoid based hierarchical nano assemblies includes - ultrathin 2D nanosheet, nanotubes, nanoribbons, helices, nanofibers, vesicles, spherical and cylindrical micelles, nano/micro flowers, 3D single crystal and some others (figure 3a)[23]. For example, Zuckermann and coworkersdeveloped free floating ultrathin peptoid nanosheet by using alternating sequence of hydrophobic and hydrophilic side chains(Figure 4a)[21,24]. Using similar Balsara and coworkers designed peptoid Vesicles at the 1 nm length scale(figure 4b)[25]. Recently, Chen and coworkers designed dynamic single-walled stiff nanotubes assembled from sequence-defined peptoids (figure 4c)[26]. Several similar types of peptoid based nanostructures are now well known in the literatures.

3. Applications of peptoid based nanostructures

Similar to other organic nanomaterials, sequence defined peptoid polymers also show unique advantages for wide applications such as better stability, low cytotoxicity along with high structural diversity with tuneable surface charges. Such advantages make peptoid based nanomaterials excellent candidates for biomaterials designing. In recent years, researchers have utilized several peptoid based nanostructures to design sensing agents, drug delivery agents, antimicrobials agents, chromatographic supports, catalyst, photodynamic therapy agents, tissue engineering, surfactants and water decontaminating agents[3,23].

4. Outlook

The above discussion covered a short overview of the sequence defined peptoids polymer as a promising tool for designing new bioinspired nanomaterials. In recent years, substantial research interestshave grown among the synthetic chemistry community to explore more such bioinspired nanomaterials for wide range of applications. However, some long standing problems are still in the region to be solved for creating well defined nanostructures. For instance, proper mechanistic details of peptoid assembly formation, role of solvents are not yet clear. Therefore, more advanced studies are yet to be done in this regard and this looks to be an important research area to work in near future.

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Series

History of Chemistry

The term protein had its origin in the earliest attempt to explain the constitution of these substances. It was in the scientific papers of Gerardus Johannis Mulder (1802-1880), a Dutch physician whose interests included nutrition and agricultural chemistry, that in 1838 the word "protein" first appeared in the chemical literature.

The term, and a statement of its derivation, appeared in two short-lived Dutch journals. One of these papers was reprinted in German translation (Mulder, 1839). In the opening sentences Mulder acknowledged his general indebtedness to Berzelius for helpful comments and advice. A few pages further on he introduced the word protein.

Gerardus Johannes Mulder

Another reference to the origin of the term protein was made by Mulder (1838) in a letter to Liebig, the substance of which was published in Liebig's Annalen. The word had been proposed to Mulder by the famous Swedish chemist Jons Jakob Berzelius(1779-1848). It was derived from the Greek adjective proteios, meaning "primarius," i.e. of the first rank or position, because it was of foremost importance for the living body.

In order to understand what Mulder wished to connote, it will be necessary to recall what was going on in the chemistry of that time. This was a period of little agreement among chemists as to the formulation of organic compounds. While the conception of the chemical atom had been clearly defined by Berzelius there was no unifying principle by which molecular magnitudes could be established. Formulas were mainly written in terms of equivalents. An immense step forward was made by Liebig and Wöhler in 1832 when they introduced the concept of the chemical radical. In their investigation of the oil of bitter almonds (benzaldehyde) they showed that a whole series of related compounds could be formulated in terms of one uniform group of atoms which they called the radical, viz: benzaldehyde, benzoic acid, benzoyl chloride, etc. This observation gave rise to an enthusiastic search for other series of compounds that could be formulated in a similarly simple fashion and led to the clear conception of organic radicals which remains to the present day. Thus it was that Mulder, who had become interested in the study of albuminous substances, attempted to fashion this new idea to proteins to achieve a more definitive characterization (Vickery and Osborne, 1928).

Jöns Jacob Berzelius

Proteins were regarded as chemical substances of great size as early as 1838 when G. J. Mulder carried out his experiments. His analyses were the first thorough studies of animal and plant protein. However, they were published mainly in a low circulation Dutch journal, and it was Berzelius, with whom he corresponded regularly, who gave a detailed account in his annual report of 1840 to the Swedish Academy of Sciences. After heating several nitrogenous or "albuminous" substances with dilute caustic soda, Mulder obtained, by neutralization with acid, a greyish-white precipitate. He noted the presence of small quantities of sulfur and phosphorus in his crude protein preparations in addition to carbon, hydrogen, oxygen and nitrogen. He concluded that the protein molecule must be huge, over 50,000, on the basis of their sulfur and phosphorus content, since each molecule had to contain at least one atom of these elements. Not until modern methods of measuring their molecular weights were developed was it possible to determine just how large they are.

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Green inhibitor as a new hope for prevention of Corrosion

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1. Introduction:

Corrosion study attracted the spotlight for researchers due to its crucial role in the world economy. About 2.5 trillion dollars can be saved by the inhibition of corrosion. One of the best methods to prevent the corrosion is to use inhibitors. In the market, large numbers of inhibitors are available. Different organic and inorganic compounds are used for these purposes. But few of them are environmental friendly. Basically appropriate inhibitor selection is not a cup of tea. Presently use of natural products like plant extracts are emerging concept to make eco-friendly planet. From this perspective, invention of a new efficient, cheap green inhibitor could be a new hope for industrialist.

1.1 Corrosion:

Corrosion is the irreversible interfacial reaction of a material (metal, ceramic, polymer) with its environment due to chemical or electrochemical reaction which results usually oxide that flake away from the base. Rusting of iron is the most common example of corrosion.

1.2 Types of Corrosion:

There are several types of corrosions is observed in our day to day life. These are given different names according to phenomenon just like general attack corrosion or uniform assault corrosion, limited corrosion, fill form corrosion, pitting, crevice corrosion, galvanic corrosion, natural cracking or atmospheric corrosion, flow assisted corrosion, intergranular corrosion, de alloying, fretting corrosion, high temperature corrosion, erosion corrosion, stress corrosion, transgranular corrosion, corrosion fatigue etc.

1.3 Theory of corrosion:

There are two theories of corrosion.

- Dry or chemical theory
- Electrochemical or wet theory

Dry Corrosion: Dry Corrosion is defined as the direct chemical attack of gases like oxygen, nitrogen and halogens which is responsible to make a solid film on the surface of the metal and protects the metal from further corrosion but if volatile or soluble corrosion is formed then the metal is exposed for further corrosion. Attack of chlorine on silver gives a protective film of silver halide whereas volatile stannic chloride formed on tin cannot prevent corrosion.

Electrochemical or wet theory: Wet corrosion defined as the electrochemical action of moisture and oxygen on metals just like rusting of iron

Mechanism of wet corrosion: we take rusting of iron as an example to understand the mechanism of wet corrosion. Two theories are proposed.

- Galvanic cell formation theory
- Differential aeration theory (concentration cell theory)

Galvanic cell formation theory: Iron piece with impurity contacted with air makes a mini galvanic cell where iron acts as anode and impurity with air forms cathode.

Anodic reaction: here oxidation reaction occurs and ferric hydroxide gives brown colour rust ferric oxide.

$$Fe \longrightarrow Fe^{2+} + 2e^-$$

$$Fe^{2+} + 2OH^- \longrightarrow Fe(OH)_2$$

$$Fe(OH)_2 \longrightarrow Fe(OH)_3$$

$$Fe(OH)_3 \longrightarrow Fe_2O_3 + H_2O$$

Cathodic reaction: this reaction depends on the composition of air contacted to electrode.

Acidic atmosphere without oxygen produces hydrogen in cathode.

$2H^+ + 2e^- \longrightarrow H_2$

Acidic atmosphere with more oxygen produces water in cathode.

$2H^+ + [O] + 2e^- \longrightarrow H_2O$

Basic or neutral atmosphere without oxygen gives OH and H2 in cathode.

$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$

Basic or neutral atmosphere with oxygen gives OH in cathode.

$2H_2O + O_2 + 4e^- \longrightarrow 4OH^-$

Differential aeration theory or concentration cell formation theory:

In several kinds of circumstances concentration cells are formed and suffer from corrosion. It depends on the diffusion rate of air or oxygen. Different amount of Oxygen reaching different parts of metal gives rise to different cathodic and anodic area. Area exposed to greater amount of air behaves as cathode and less exposed to air behaves as anode and the anode preferentially corrodes.

The anodic reaction is Fe $\longrightarrow Fe^{2+}$ +2e-

The reaction taking place in cathode is

H_2O +1/2 2e- $\longrightarrow$ $2OH^-$

Fe^{2+} 2OH - $\longrightarrow$ $Fe(OH)_2$

It is further oxidised to $Fe(OH)_3$. Due to large anodic area corrosion is more concentrated at anode.

1.4 Measurement of corrosion:

Weight loss method, open circuit potential method, linear polarisation technique, half cell potential monitoring are some common methods to measure corrosion quantitatively.

2. Importance of the study of Corrosion:

Corrosion affects our daily life directly or indirectly which sometimes carries a bigger loss to us.

- Economic loss: corrosion causes piping, vessels and tanks to become brittle and less ductile. Corrosion products deposited on surface make a complicated maintaince and construction collapse. Replacement of tanks, pipe or vessel bears a great economic loss.

  According to WCO, A loss over US $2.5 trillion dollars is caused to global economic every year due to corrosion. In India, according to NACE, it causes 40 billion loss in a year due to corrosion.

- Safety: it may penetrate tanks and vessels containing fluids and it leads to the leakage of fluids which may lead accident and a threat to our environment..

3. Corrosion inhibitor:

Now it has been observed that with the proper corrosion prevention technologies about 30% of the loss can be avoided. One of the best method is to use inhibitor which can decrease the corrosion rate. A corrosion inhibitor is a chemical compound that when added to liquid or gas decreases the corrosion rate of a material typically a metal or an alloy. The effectiveness of the corrosion inhibitor depends on the fluid composition, quantity of water and flow regimes.

3.1 Characteristics of inhibitor:

- ✓ The inhibitor should be available and stable.
- ✓ It should be nontoxic and better to become eco friendly.
- ✓ It should be less expensive.

Inorganic or Organic both compounds can be acted as inhibitor. But compounds containing nitrogen, phosphorous oxygen or sulphur are effective as corrosion inhibitor.

Cause of decrease of corrosion rate:

- ✓ Adsorption of ions or molecule into metal surface.
- ✓ By increasing or decreasing the anodic or cathodic reaction.
- ✓ Decreasing the electrical resistance of metal surface.

4. Green inhibitors in corrosion study:

The concept of green inhibitor was invented in the middle half of 19th century. In 1960, Baldvin et al. 1st made research in the field of corrosion by using vegetable oils as the inhibitor of steel in acid pickling process. Mainly extracts from different parts of trees is used as green inhibitors because Plant extracts are found to be rich sources of phytochemicals which can be a good substitution for traditional toxic inhibitors. Leaves extract has been in the centre of interest of researcher due to its high content of phytochemicals compare to the other parts of the trees. As so far, Bamboo leaves extract, black pepper extract, *Murraya koenigii* leave extract, Olive leave extract, Mango, Orange, passion and Cashew peel extract, *annas stavium* leave extract, *Pactin terrestrial* plant extract and *Ver monia amygdalina* (bitter leaf extract) are some reported good green inhibitors. Mango/Orange peels, Aloe leaves, *Azydracta indica, Auforpio curkiale, Gracinia kola* seeds, banana peels *(Musa sapientum), Lawsonia extract* (Henna), Elcalyptus oil, *Terminalia bellerica, Emblical officinals* also have shown an excellent inhibitory action towards different acid pickling processes. The methanolic leave extraction of *Magnifera indica* (mango) has been reported as a good corrosion inhibitor due to presence of polyphenols, flavonoids and Xanthanones which shows excellent antioxidant, antiflammatory and allopathic effects.

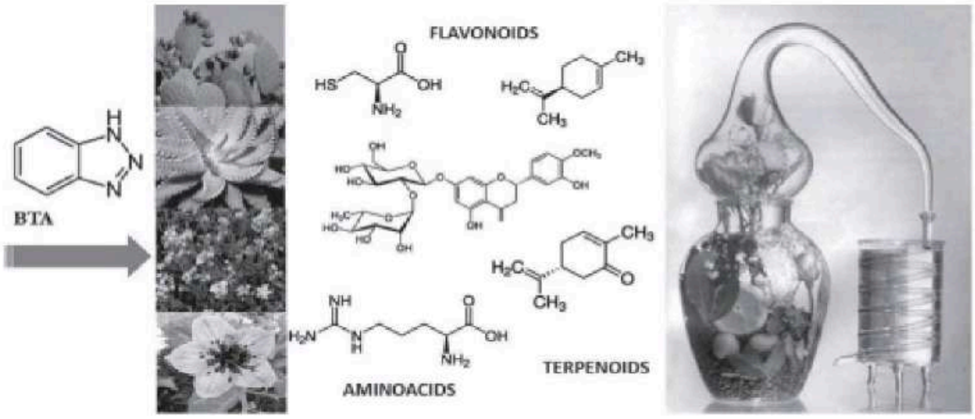

Fig 1: Some green inhibitors with its components.

In this process, adsorption takes place to slow down the detoriation process. This may be physical adsorption or chemical adsorption. The unshared pair of heteroatom and the conjugated double bond plays a vital role in the interaction with the metal which slows down the anodic or cathodic reaction or diffusion of aggressive species of the metal and decreasing the electrical resistance of the substance.

In the first step, adsorption of organic inhibitor on the metal surface usually occurs by replacement of one or more water molecules initially adsorbed at metal surface.

$$\mathrm{Inh(sol)} + x\mathrm{H_2O(ads)} \longrightarrow \mathrm{Inh(Ads)} + \mathrm{H_2O(soln)}$$

Where Ins represents the inhibitor and x is the no. of molecules is displaced by inhibitor. The inhibitor may combine with the newly generated M2+ ions to give metal-inhibitor complex.

$$\mathrm{M} \longrightarrow \mathrm{M^{2+}{+}2e^-}$$

$$\mathrm{M^{2+} + Inh(ads)} \longrightarrow \mathrm{(M\text{-}Inh)^{2+}(ads)}$$

Depending on the relative solubility of the resulting product it can further catalyse or inhibit metal dissolution process. In presence of inhibitor the active sites of metal almost blocked by the adsorption of inhibitor which makes a passive layer suppressing the further corrosion. The performance of chemical inhibitor depends on the chemical structure physiochemical properties of the compound like functional groups, electron densities on donor atoms, p orbital character and the electronic structure of the molecule. It also depends on the factors like chain length of the compound, size of the molecule, bonding, nature of the molecule aromatic/conjugate or aliphatic, change on bonding to the substrate, cross linking ability, solubility in the environment, charge of the metal, steric effects etc.

4.1 Advantages of green inhibitor:

- ✓ They are biodegradable.
- ✓ Do not contain any heavy metal.
- ✓ Eco friendly and non toxic.
- ✓ Easily available and inexpensive.

5. Conclusion:

Though till date, the efficiency of green inhibitor is less than synthetic inhibitor though green inhibitor is cheaper than synthetic one. But sufficient research on green inhibitor has not been carried out. More research and information of plants is required to find out efficient green inhibitor which can bring a revolutionary change in industry.

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Students' Section

Anti-Viral Drugs-A brief introduction

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Drugs that are useful in tackling viral diseases where there is a lack of an effective vaccine, or where infection has already taken place are known as antiviral drugs. The first antiviral agent appeared only in 1960s and till 1980s only three clinically useful antiviral drugs were in use. The early antiviral drugs included idoxuridine and vidarabine for herpes infection and amantadine for influenza A.

A variety of factors make the design of effective antiviral agents difficult, including their ability to undergo antigenic changes, the latent period during which there are no symptoms, and their reliance on host enzyme and other processes. This problem is further compounded by the fact that host immunity is not well understood and that symptoms of viral infection may not appear until replication is complete and the viral genome has been incorporated into infected cells.

Antiviral compound have been designed in eight general areas. They are:

- Agents that disrupt virus attachment to host cell, receptor, penetration, or uncoating.
- Agents that inhibit virus associated enzymes, such as DNA polymerase and others.
- Agents that inhibit viral transcription.
- Agents that inhibit viral translation.
- Agents that interfere with viral regulatory proteins.
- Agents that interfere with glycosylation, phosphorylation, sulfation and so on.
- Agents that interfere with assembly of viral proteins.
- Agents that prohibit the release of viruses from cell surface membrane.

Most of the antiviral drugs in use today act against HIV, herpes viruses (responsible for a variety of ailments including cold sores and encephalitis), hepatitis-B and hepatitis-C. As regards mode of action most antiviral drugs in use today disrupt clinical stages of the virus life cycle or the synthesis of virus-specific nucleic acids.

Herein a glimpse of some of the antiviral drugs is as follows:

Antiviral therapy against HIV

HIV is an example of a group of viruses known as the retroviruses.

At present, most drugs that have been developed act against the viral enzyme reverse transcriptase and protease. However, a serious problem with the treatment of HIV is the fact that the virus undergoes mutation extremely easily. This results in rapid resistance to antiviral drugs. It is found that the treatment of HIV with a single drug has a short-term benefit, but, in long term, the drug serves only to select mutated viruses which are resistant. As a result current therapy involves combinations of different drugs acting on both reverse transcriptase and protease. This has been successful in delaying the progression to AIDS and increasing survival rates. Further improvements in HIV treatment have resulted from the development of drugs against other viral targets, such as integrase.

Some of the anti-HIV agents are Zidovudine (AZT, ZDV), Didanosine (ddl), Zalcitabine(ddC), Lamivudine, stavudine, etc.

Antiviral drugs against Hepatitis-C

Hepatitis-C virus (HCV) is a positive single-stranded RNA viruses. It is a blood-borne virus that can cause serious liver-damage, cancer and death.

Hepatitis-C virus is treated using direct acting antiviral (DAA) tablets. DAA tablets are the safest and most effective medicines for treating hepatitis-C. NHS (National Health Service) approved hepatitis-c medicines include:

- Sofosbuvir
- A combination of ledipasvir and sofosbuvir
- A combination of ombitasvir, paritaprevir and ritonavir taken with or without dasebuvir
- Ribavirin, etc.

Antiviral drugs against Hepatitis-B

Hepatitis-B virus (HBV) is classified as a hepadnavirus with a double-stranded, circular DNA genome. HBV establishes chronic infections especially in infant and are at high risk of developing hepatocellular carcinoma.

Antiviral medications include entecavir (Baraclude), tenofovir (Viread), lamivudine (Epivir), adefovir (Hepsera) and telbivudine (Tyzeka), etc.

Antiviral drugs against Herpes virus

The herpes virus family contains several of the most important human pathogens and is responsible for causing a spectrum of common disease. A common and significant feature of herpesvirus is their ability to establish lifelong, persistent infections in their hosts and to undergo periodic reactivation.

There are a number of antiviral medications with activity against HSV-1 and HSV-2. With the exception of foscarnet and cidofovir, all are nucleoside analogous. While three of these medications (acyclovir, famiciclovir and valaciclovir) are used to treat the overwhelming majority of cases of HSV-1 and HSV-2, acyclovir is most active against HSV.

Antiviral drugs against Covid-19

The disease Covid-19 was caused by the virus SARS-CoV-2. In human, the transmission of SARS-CoV-2 can occur via respiratory secretions (directly through droplets from coughing or sneezing or indirectly through contaminated objects or surfaces as well as close contact.

Molnupiravir is the first oral direct-acting antiviral shown to be highly effective at reducing nasopharyngeal SARS-CoV-2 infectious virus. Remdesivir is the antiviral drug that is approved by Food and Drug Administration (FDA) for the treatment of Covid-19. Ritonavir-boosted nirmatrelvir (Paxlovid), certain anti-SARS-CoV-2 monoclonal antibodies (mAbs) have received emergency use authorization from Food & Drug Administration.

In the recent years, considerable progress has been made towards the designing of antiviral drugs. Though it is difficult to design an effective antiviral drug, more than 90 antiviral drugs have been approved in between June 1963 and April 2016 to treat nine human infectious diseases. Now a day's antiviral drugs are designed as a combination of different drugs to increase the survival rates by decreasing resistance to antiviral drugs as viruses undergoes mutation extremely easily. Designing of antiviral drugs possess one of the greatest challenge to mankind.

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A sustainable battery with a biodegradable electrolyte made from crab shells

Vast quantities of batteries are being produced and consumed, raised the possibility of environmental problems. For example, polypropylene and polycarbonate separators, which are widely used in Lithium-ion batteries, take hundreds or thousands of years to degrade and add to environmental burden. Batteries uses an electrolyte to shuttle ions back and forth between positively and negatively charged terminals. Anelectrolyte can be liquid,paste, or gel, and many batteries use flammable or corrosive chemicals for this function. A new battery, which could store power from large scale wind and solar sources, uses a gel electrolyte made from a biological material called chitosan. Chitosan is a derivative product of chitin. Chitin has a lot of sources, including the cell walls of fungi, exoskeleton of crustaceans, and squid pens which can be easily obtained from seafood waste. A biodegradable electrolyte means that about two thirds of the battery could be broken down by microbes. The chitosan electrolyte broke down completely within five months which leaves behind the metal component zinc which could be easily recycled. The zinc and chitosan battery has an energy efficiency of 99.7% after 1000 battery, making it a viable option for storing energy generated by wind and solar for transfer to power grids.

New catalyst leads to more efficient butadiene production

Creating butadiene form butane is tricky. Existing techniques for converting butane into butadiene either create a bunch of byproducts that nobody wants, or convert only a small fraction of butane into butadiene each time the butane passes through the chemical reactor. As a result, we have to run the butane through the same process repeatedly. This is an expensive process in terms of both energy and money because after every pass through the chemical reactor, we have to separate the butadiene and byproducts form the butane which takes a lot of energy and run the butane through the reactor again. The researchers have engineered a catalyst that converts more butane into butadiene with each pass through the reactor and the word was done using an oxidative dehydrogenation reaction. The catalyst is a lithium bromide shell surrounding a core of lanthanum strontium ferrite. The reaction requires a modular reactor, and the conversion takes place at between 450 and 500 degrees Celsius.

2D boundaries could create electricity

A new study describes the discovery of piezoelectricity- the phenomenon by which mechanical energy turns into electrical energy across phase boundaries of two-dimensional materials. The discovery could aid in the development of ever smaller nanoelectromechanical systems, devices that could be used, for example, to power tiny actuators and implantable biosensors, and ultrasensitive temperature or pressure sensors. The researchers show the atomically thin systems of a metallic domain surrounding semiconducting islands creates a mechanical response in the material's crystal lattice when subjected to an applied voltage. The presence of piezoelectricity in 2D materials often depends on the number of layers, but synthesizing the materials with a precise number of layers has a been a formidable challenge. We have to make a one-dimensional, metal-semiconductor junction in a 2D heterostructure, thus introducing crystallographic as well as charge asymmetry at the junction. The lateral junction between phases is very interesting, since it provides atomically sharp boundaries in atomically thin layer which allows to engineer materials in 2D to create device architectures that could be unique in electronic application. The junction is less than 10 nanometer thick and forms when tellurium gas is introduced while molybdenum metal forms a film on silicon dioxide in a chemical vapor deposition furnace. The process creates islands of semiconducting molybdenum telluride phases in the sea of metallic phases. Applying voltage to the junction via the tip of piezoresponse force microscope generates a mechanical response. That also carefully measures the strength of piezoelectricity created at the junction. The difference between the lattice structures and electrical conductivity creates asymmetry at the phase boundary that is essentially independent of the thickness. That simplifies the preparation of 2D crystal for application like miniaturized actuators.

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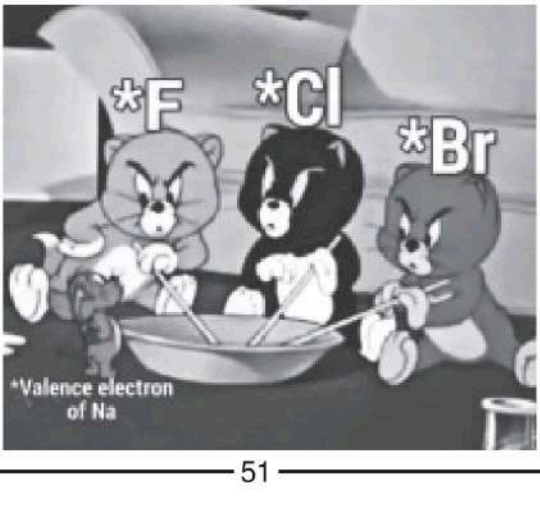
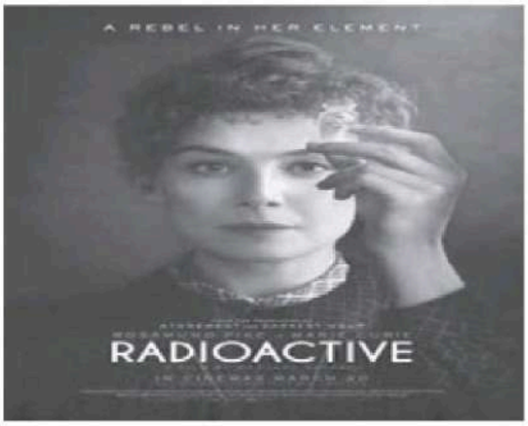


CHEMISTRY IN MOVIES

Science and technology has been a hot topic in the world of movies, chemistry is no exception. In recent times, makers have come up with many gripping story lines based on or related to the subject of Chemistry. With the growth of OTT platforms a variety of content can be seen nowadays, content related to science are on the rise these days. It is said that the field of Chemistry is vast, movies are no exception. Let us quickly go through some movies/series which have brought chemistry to our screens. As students of chemistry, watching these movies will surely compel you to analyse the scopes of the subject and at the same time motivate to explore the subject.

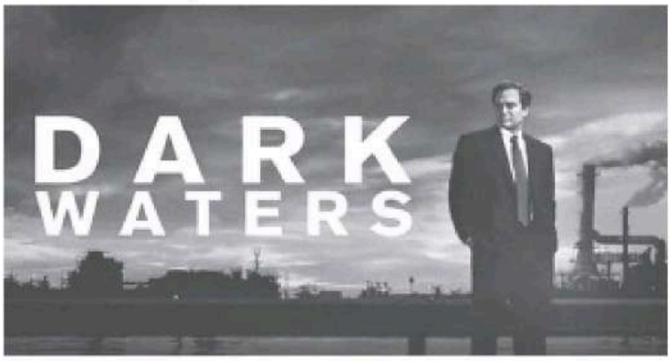
1. RADIOACTIVE

This is perhaps the second time and most recent after "madam curie" from 1943 that someone has tried to bring the biography of one of the greatest scientists, the world has known ,into the screens . Directed by Marjane Satrapi, Radioactive is the incredible true story of Marie sklodowska-curie and her Nobel prize winning work that changed the world. The movie also portrays the personal life and struggles that she went through. Besides key moments in her life , the good and bad usages of her discovery appear throughout the film. Although a little dramatic, this movie will give a insight into her adventurous life. It is available in Amazon Prime.



2. DARK WATERS

DARK WATERS released in 2019 is another movie which portrays the effect of chemistry on everyday life. Although it is a legal thriller there is a significant emphasis on chemistry. Dark Waters is a 2019 American legal thriller film directed by Todd Haynes and written by Mario Correa and Matthew Michael Carnahan. The story dramatizes Robert Bilott's case against the chemical manufacturing corporation DuPont after they contaminated a town with unregulated chemicals.



The movie highlights the adverse effects of chemicals on nature and exploitation by big corporate. It also raises concerns on water pollution which often goes unnoticed.

Everyone should give it a watch to understand the seriousness of environmental damages caused by chemicals.

And think about the prospect of green chemistry.

3. Chernobyl

This name is not new to the audience and the name itself is enough to give chills. The horror and tragedy of the Chernobyl nuclear accident is still afresh.

"Chernobyl "released in 2019 , tells the powerful and visceral story of the worst man made accident in the history. Although the radiation scenes might be disturbing to some but it will make us think twice about the proper and safe use of technology. This reminds us about the enormous power of nuclear chemistry . It is also a must watch series which will make you realize the potential that chemistry possess. This series will raise the question on boundaries of science.

■ ■ ■

A focus on chemistry could see future solar panels reach their potential

A material that has been heralded as the key to producing more efficient next-generation solar panels.

A Team at university of Surrey found that fusing perovskite materials with an element called ferrocene aromatically seems to increase the efficiency of perovskite based solar panels. The research done scales these perovskite cells to a minute level, focusing on the chemical compound and their specific problems. Normally, the cells were coated and doped in Lithium but Lithium absorbs water, increasing energy deficiency over time.

The teams discovered an element within organometallic chemistry called ferrocene that significantly improves efficiency and stabilises the drop in energy that all solar panels have over time. It is also cheap to produce and solves the water absorption proscem.

Perovskite materials are widely considered to be the successor to silicon because they are lightweight and for cheaper to produce. However, the premise of perovskite has yet to be realised because of the difficulty of replicating lab result in mass production.

"Ferrocene" has been proved to be a very important material that can be used for the future of solar Panel. It is also a precursor to iron nano particles, can be also used as a catalyst for the production of carbon nanotubes.

The Development achieved by the team at University of Surrey can be highly beneficial to upgrade to a solar powered future and decrease the load on fossil fuels.

AMAZING FACTS

1. The metal Gallium can melt in the hand. Its melting temperature is 29.8° C.
2. A liter of sea water contains 35 grams of salt.
3. Natural gas has no colour or smell.
4. The first synthetic dye produced by human beings was mauveine.
5. If you exposed a glass of water to space , it would boil rather than freeze.
6. If you pour a handful of salt into a full glass of water, the water level will actually go down rather than overflowing the glass.
7. The rarest naturally occurring element in the Earth's crust may be astatine. The entire crust appears to contain about 28 grams of the element.
8. Bee stings are acidic, while wasp stings are alkaline.
9. Airbags in cars are manufactured with Sodiumazide,that is a very poisonous chemical.
10. Although the temperature is the same, the water feels colder than air, as water is the better conductor of heat and acts as a thermal insulator.

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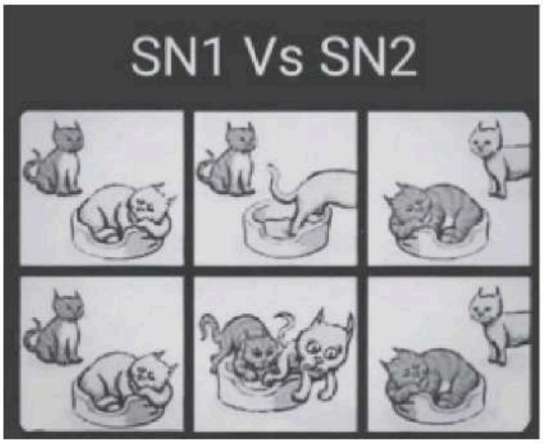

Chemistry Puzzle

EXTREME COMMON MEDICINE NAME WORD SEARCH

A	Q	T	I	L	Z	T	F	D	U	Y	F	R	D	V
C	L	S	A	J	N	I	A	R	D	S	B	E	T	G
Y	R	P	C	S	F	Y	D	S	R	A	I	S	G	H
C	M	I	H	B	P	C	T	O	P	H	Y	D	D	E
L	I	D	M	E	J	Q	E	M	V	A	T	C	A	P
O	J	H	I	U	N	B	U	N	K	U	R	V	P	A
V	M	I	T	G	V	O	V	H	Z	M	D	B	S	R
I	I	E	B	N	A	M	B	M	F	R	E	I	O	A
R	R	Y	Z	U	L	N	T	A	S	I	W	W	N	C
D	I	A	Z	E	P	A	M	J	R	D	Q	A	E	E
A	S	R	T	Y	H	R	G	F	V	B	H	W	H	T
D	G	M	N	I	J	K	O	J	H	U	I	Q	J	A
R	I	M	J	I	M	V	B	F	T	L	B	T	K	M
N	Q	V	U	F	P	F	G	U	E	A	B	O	A	O
L	I	S	O	T	N	O	R	P	Y	N	M	I	N	L

Listed here are the common names of few organic pharmaceutical compounds. Find them in the grid above :

ACYCLOVIR
DIAZEPAM
DAPSONE
IBUPROFEN
PRONTOSIL
ZIDOVUDINE
PHENOBARBITAL
PARACETAMOL

Chemistry Crossword

$^{1.}$A	R	R	H	E	N	I	$^{2.}$U	S										
							S											
							A											
							N											
							O											
							V											
							$^{3.}$I	O	N	I	$^{4.}$C				$^{10.}$L			
							C				O				E			
							H				V				V			
					$^{6.}$F						A				E			
					R						$^{7.}$L	U	X	F	L	O	O	D
^{5}S	Y	M	B	I	O	S	I	S		$^{9.}$L	E	W	I	S	I			
					N						N				N			
					T						T				G			
					S													
					T													
					R													
					A													
					I													
		Y	T	I	N	I	F	F	A	N	O	T	O	R	P$^{8.}$			

1. According to ___________ definition, acids are H^+ donor and bases are OH^- donor. (ROW)

2. __________, stated that acids give up cation and accept anions whereas the vice-versa for bases. (COLUMN)

From HSAB principle,

3. Hard-Hard interactions are _______ (ROW)

4. Soft-Soft interactions are ______ (COLUMN)
5. Effect where addition of soft substituents can soften a hard centre and hard substituent can reduce softness. (ROW)
6. The effect where bulky substituents affect stability of acid-base adduct due to steric hindrance. (COLUMN)
7. According to ___________ definition, acids are oxide acceptor and bases are oxide donor. (ROW)
8. The most fundamental measure of inherent basicity of species is _______ (ROW)
9. According to ___________ definition, bases are electron pair donor and acids are acceptor. (ROW)
10. The effect in which acids tend to become indistinguishable in strength when dissolved in strongly basic solvent owing to the ge=reater affinity of strong basses for protons. (COLUMN)

N.B. Please send the answer to The Editor, 'The Chemical Axis', Department of Chemistry, B. Borooah College, Guwahati, Assam - 781007 on or before 01-10-2022
E-mail : thechemicalaxis@gmail.com

Any suggestion regarding the improvement of 'The Chemical Axis' will be solicited.
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7. Period of study :
8. Course of study (PG/UG/HS) :
9. Any suggestion regarding development of the Forum :

Date :
Place :

Signature

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