

TRENDS IN SUSTAINABLE CHEMISTRY

Editor

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POST GRADUATE DEPARTMENT OF CHEMISTRY

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NATURAL PHOTONIC MATERIALS AND BIO-INSPIRED PHOTONIC CRYSTAL SENSORS

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INTRODUCTION

The magnificent colours of butterflies and peacocks with intense iridescence and metallic glossiness are a fascination for all of the nature lovers. But, till 17th century, it was believed that these beautiful colors are due to chemical colors like that of dyes and pigments. However, this concept could not explain the existence of blue color in nature. Later, the researchers have proved that apart from chemical coloration, various other mechanisms can impart coloration in nature, and the most interesting reason behind is structural coloration. In 1665, Hooke published a book explaining the structural color existing in nature.¹ He suggested that the color of peacock feather is the alternate arrangement of solid material and air. The structural colors are, in fact, the upshot of intricate and intelligent manifestations by nature with well-defined microscopic structures and hence proper clarification for the development of structural color was obtained only after the development of Scanning Electron Microscope (SEM).² First attempt was made by Frank and Ruska in 1939 by explaining the mechanism behind the blue colored feathers of ivory breasted pitta using electron microscope.³ Later in 1942, Anderson et al. and Gentil reported that the complicated structure on the tiny scale of Morpho butterfly is responsible for its beautiful color and this in turn, accelerated structural studies at the nanometer scale.^{4,5} Another fascinating structural color was that of opals which remained a great mystery until C. V. Raman and Jayaraman in 1953 gave the correct explanation for it.⁶ They explained that the periodically varying refractive index due to the regular array of silica particles gives the magnificent colors to opal, and later, Sanders proved it with electron microscopy.⁷

The pigments and dyes show color due to the exchange of energy between light and electron, where electrons are excited to higher energy levels. However, structural color is due to fundamental optical processes such as reflection, refraction, interference, diffraction, scattering, etc.³ Color of the sky, bright color of many animals (e.g. wings of butterfly, barbules of peacock tail feather, etc.), and iridescent color of soap bubbles are some of the typical examples for structural color (**Figure 1**). Structural color can be classified into iridescent (angle-dependent structural color) or non-iridescent color (angle-independent structural color), where the former is changed with respect to the viewing angle and latter remains identical regardless of viewing angle. For example, iridescent color can be produced by interference or diffraction, whereas non-iridescent structural color can be seen by light scattering.³ Considering the physical mechanisms of structural coloration, both interference and diffraction can give rise to angle-dependent structural colors by regularly arranged micro or nano structure, and some forms of scattering can give rise to angle-independent structural color by irregularity of the micro or nano structure.³ Unlike, relatively toxic pigmentary

colorations, structural color is bright and resistant to photobleaching. These findings helped in the development of a new area of research based on colloidal photonic crystals (PC), an important candidate for structural color materials.

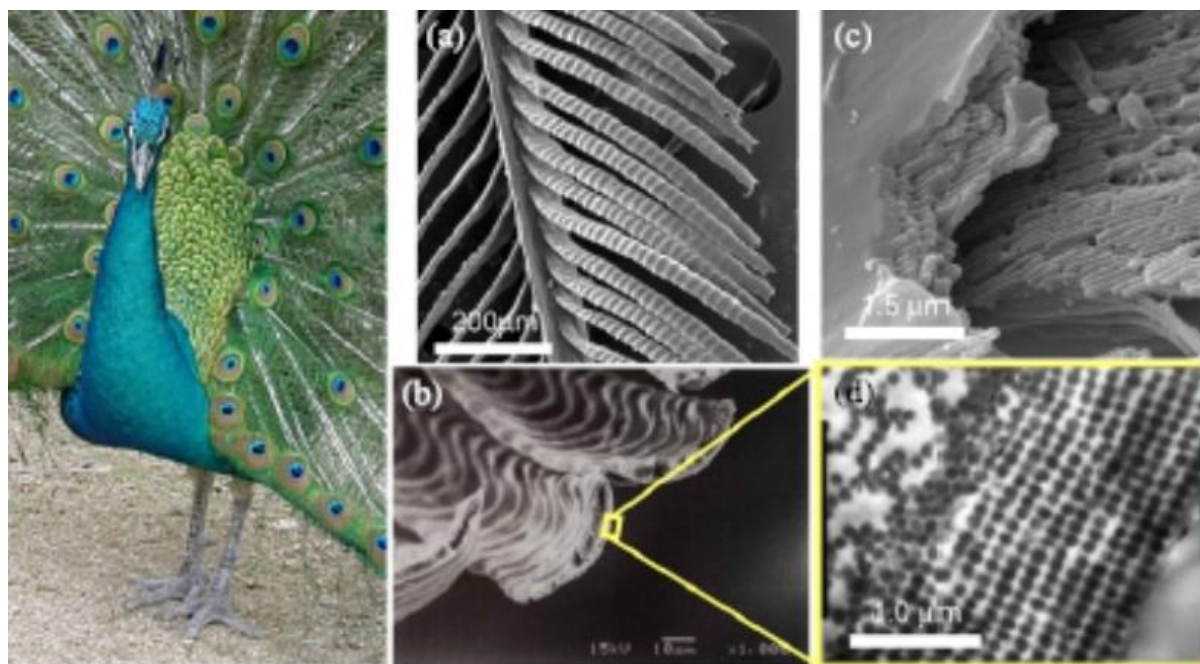


Figure 1. A typical example for structural coloration: Peacock (Indian peafowl). A feather of the peacock consists of many barbules sticking out from a main shaft and each barbule has a lot of barbules. SEM images of (a) barbules, (b) the cross section and (c) interior of a barbule. (d) TEM image of the cross section of a barbule.⁸

PHOTONIC CRYSTALS (PCs)

Photonic crystals (PCs) were originally introduced by Yablonovitch and John in 1987. A typical PC consists of periodic arrangement of dielectric material, which induces periodic modulation of the refractive indices (RI).^{9,10} They could have periodicity or direction of modulation of refractive indices in one (1D), two (2D), or three dimensions (3D). **Figure 2.1** illustrates three configurations of PCs with different periodicities.¹¹ Even though the repeating units are colorless, their periodic organization imparts coloration to PC. The fundamental optical process in the coloration mechanism of a typical PC is diffraction on the length scale of the wavelength of the incident light. The diffraction of incident light by the periodic arrangement in PC architecture provides a range of electromagnetic waves being prohibited from propagating through it and thus, it is diffracted (Figure. 2.2).¹² This region of electromagnetic waves, namely Photonic Band Gap (PBG) provides a potential platform for controlling the propagation of light. Due to the presence of different dielectric media and refractive index contrast, light is scattered and/or diffracted at PBG, where interference of the scattered waves is destructive in all directions. The main advantage due to the existence of PBG is structural coloration. Extensive studies on PBG have resulted in the development of many photonic devices based on PCs capable of confining, controlling, and routing the light in a photonic chip.¹³ PCs also find application as platforms for chemical and biological sensors by enhancing the light-matter interaction through the slow photon effect.

STIMULI RESPONSIVE PCs IN NATURE

Nature also resides some interesting structural colors that change in response to the stimuli from surrounding environment. Common examples are chameleons, Paracheirodon innesi,

paradise whiptail, blue damselfish, tortoise beetle, hercules beetle, *etc.* In these creatures, the lattice spacing changes in response to the external stimuli and thus shifting the diffracted waves towards blue or red. Chameleons are well-studied stimuli-responsive natural PCs, and they show variable structural color during social interaction. The dynamic color change of panther chameleons was extensively studied by Teyssier *et al* and showed that the variations in the spacing of guanine nanocrystals within a superficial thick layer of dermal iridophore cells facilitate the stimuli-responsive behavior.¹⁴ **Figure 3a** and **b** show the reversible color change of a male chameleon during the relaxed and excited state, the corresponding TEM images in **Figure 3c** and **d** validate the stimuli-responsive behavior by active tuning in the lattice spacing.

The natural structural arrangements resulting in responsive color has been mimicked by researchers via fabrication of colloidal photonic crystals. The development of stimuli-responsive PC offers a potential platform for both chemical sensing and biosensing.

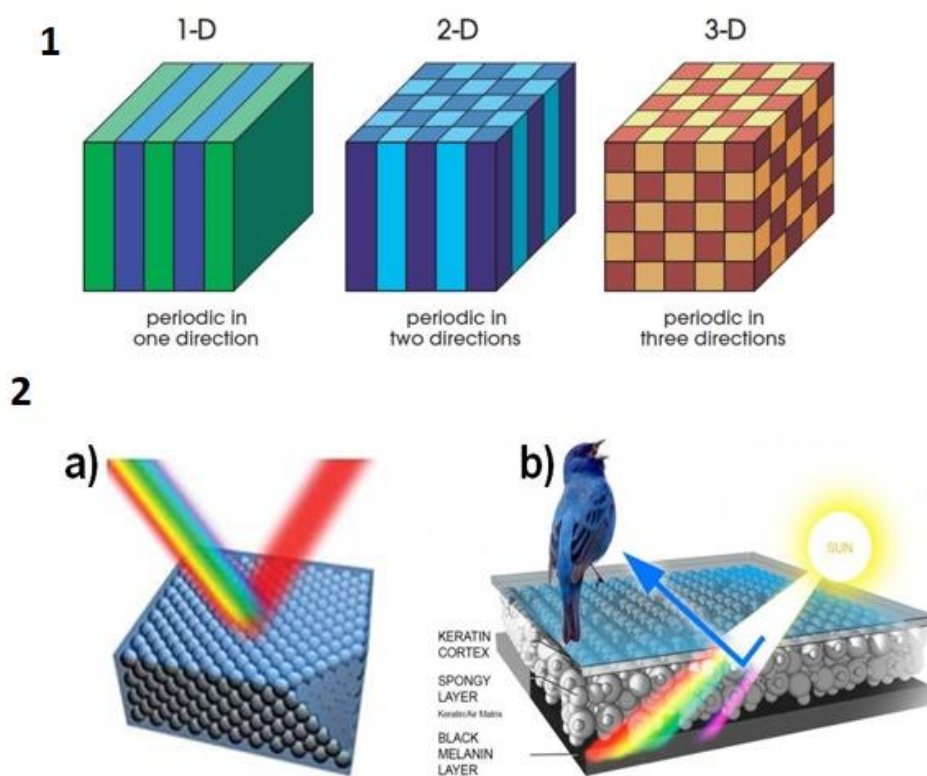


Figure 2. (1) Schematic representation of 1D, 2D and 3D photonic crystals.¹¹
 (2) a) Schematic of diffraction of incident light wavelength in a typical PC at PBG and
 b) Blue coloration of a bird due to the existence of PBG at blue color.¹²



Figure 3. a), b) Photograph of reversible color change of a male chameleon during relaxed and excited state, c) and d) corresponding TEM images showing the changes in lattice spacing.¹⁴

STIMULI-RESPONSIVE PCs FOR SENSING APPLICATION

In stimuli-responsive PCs, PBG and hence the structural color of a PC can be altered by changing the refractive index or lattice spacing. Stimuli-responsive PCs can be created in two ways. In one approach, when a stimulus (for example solvent) is infiltrated into the voids of CC, and the resulting changes in the effective refractive index can cause PBG shift. Another way to induce color change is by incorporating stimuli-responsive material into the PC structure. For example, hydrogels are an important candidate for stimuli-responsive polymeric material, which can undergo volume phase transition by swelling or deswelling. The schematic representation in **Figure 4** depicts the stimuli-response of a PC by changes in lattice spacing (d) via the swelling mechanism.¹⁵

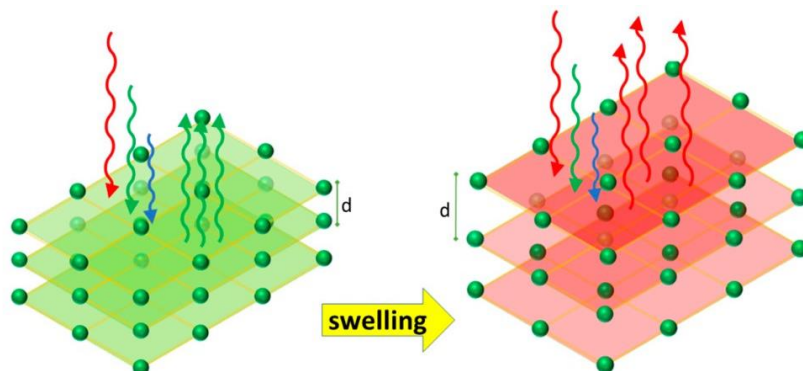


Figure 4. Stimuli-response of a PC by changes in lattice spacing via swelling or deswelling mechanism.¹⁵

Based on responsive photonic crystals (RPCs) several sensing platforms have been developed towards external stimuli like humidity, temperature, pH, solvents, mechanical force, biomolecules, electric fields, magnetic fields or light. Interestingly, PBGs of RPCs can be tuned over the entire visible spectrum and can specifically prepare PCs of desired color. Thus the major advantage is that the color change in the developed sensor can be perceived directly with our naked eyes. This makes the detection method more simple and reliable. For instance, Hawkeye *et al.* developed a humidity sensor with TiO₂ based 2D PC comprising high density and low density layers.¹⁶ This in turn, created high and low refractive index layers and the change in effective refractive index resulted in a visible structural color change in response to relative humidity as shown in **Figure 5 B**.

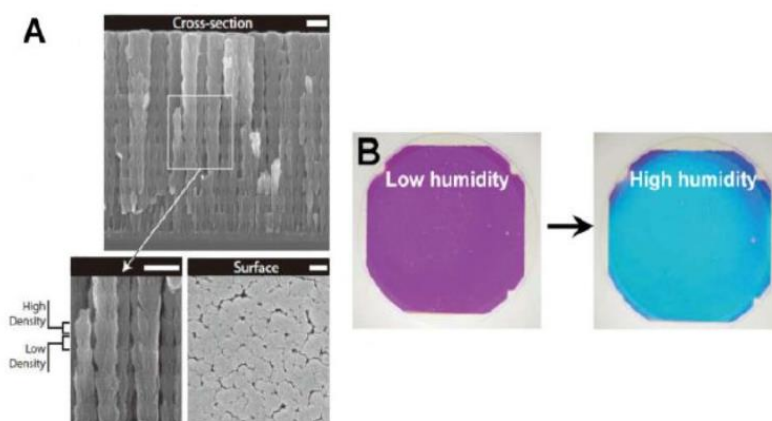


Figure 5. A. Top view and cross-sectional view in the SEM images of 1D TiO₂ PC films. B. Photograph of sensor under low and high humidity environments.¹⁶

CONCLUSION

The chapter summarizes the mechanism behind fascinating structural colors in nature and also explains the way of mimicking these nanostructures for the development of sensors. Still, bio-inspired structures remain a hot topic for the researchers and have developed several chemical and biological sensors based on responsive photonic crystals. New fabrication methods are also underway for the fabrication of bio-inspired photonic sensors.

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NANOCELLULOSE AS GREEN PLATFORM FOR FUNCTIONAL HYDROGELS/AEROGELS

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INTRODUCTION

Sustainable nanomaterial synthesis and their materialization is the outset of modern nanotechnology. Nanocellulose, for the last decades, has become the active area of research for being the greenest material that could be derived from inexhaustible bioresources, possessing invincible properties. The unique combinations of properties by virtue of adaptive functionalities makes them tunable platform that outperform most of the present days synthetic material for myriad of applications.

MACROCELLULOSE TO NANOCELLULOSE

Nanocellulose is a general terminology used for cellulose having at least one dimension in nano regime. The source could be a plant or its any part (bast, fruit, seed, leaf, etc), some marine organisms, like certain algae, tunicates etc. and even obtained from certain bacteria as their extracellular product. The morphological level understanding of cellulose mainly unravels how the elementary cellulose bundles or ensembles are arranged within the cell wall. Apparently, as the size approaches to the macro level, the structural interpretation becomes more complex. In native cellulose, the fibrillar units are organized in layers with varying textures. Simply stated, a macro structured cellulose fiber comprises of a well-organized architecture of cellulose fibrils. The supramolecular level structure of cellulose broadly covers the arrangements/ assembly of individual linear chains in the native structure. An elementary fibril is considered to be the smallest morphological unit, which bundle into microfibrils (nanocellulose fibers, NCF) with size ranges around 3-25 nm (vary source-to-source). An illustration of the hierarchical architecture of cellulose fibrils is given in **Figure 1**. These microfibrils are again arranged in an even complex way along with various non-cellulosic cementing agents within the cell wall. A typical hierarchical arrangement of NCF bundles within the cell wall along with lignin, pectin, hemicellulose, etc. are schematically represented in **Figure 2**. Thus, the isolation of NCFs from lignocellulosic fibers involves the removal of all the above-mentioned residues.

TYPES OF NANOCELLULOSE

Nanocellulose, based on its isolation methods, cellulosic source, aspect ratio, etc. vary in their structure, properties and functions. Based on these factors they are variously termed as nanocrystals, nanowhiskers, nanorods, microfibrils or nanofibers, microbial cellulose, etc. Each microfibril consists of statistically alternated crystalline and non-crystalline regions (**Figure 3**). The cellulose chain orientation in these regions are mainly governed by the spatial interactions like hydrogen bonding, Van der Waals interaction, etc. and is largely vary depending upon the origin and modes of isolation.

NC is mainly classified into three subcategories, nanocellulose crystals (NCCs), nanocellulose fibers (NCFs) and bacterial cellulose (BC) (**Figure 3**). NCC is a rod/whisker-like material derived from native cellulose by removing amorphous regions leaving behind the crystalline parts, whereas, NCFs retain most of its amorphous part during the cleavage of hydrogen bonds resulting in nano-sized fibers with high aspect ratio. While both NCCs and NCFs are obtained by top-down synthetic approaches, BC is produced by bacteria *via* a bottom-up approach. *i.e.*, BC is biosynthesized by certain bacteria in the form of high aspect ratio nanofibers/nanoribbons entangled at the water/air interface under favourable culturing conditions.

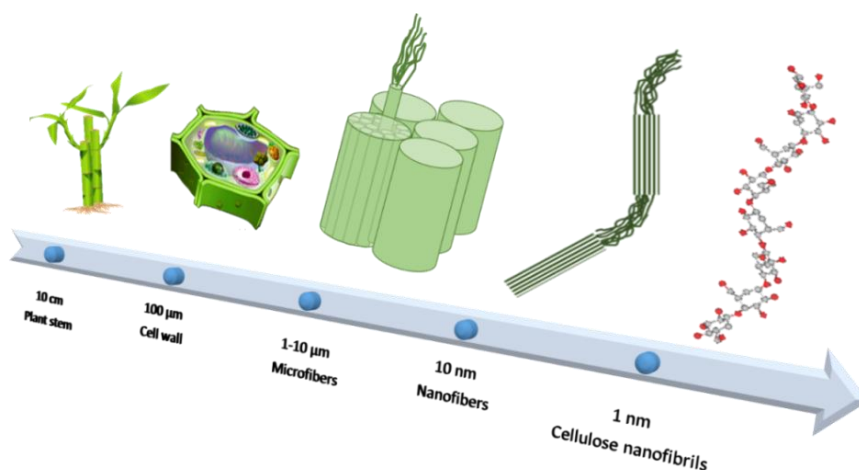


Figure 1. Figurative illustration of existence of cellulose in plants.

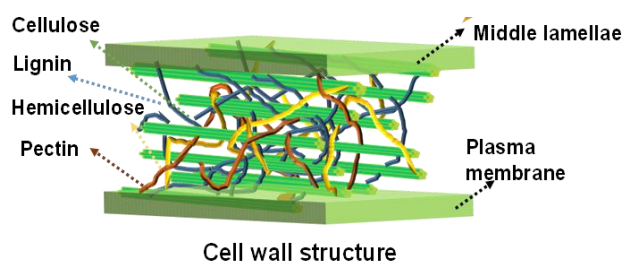


Figure 2. Schematic illustration of the hierarchical structure of plant cell wall.

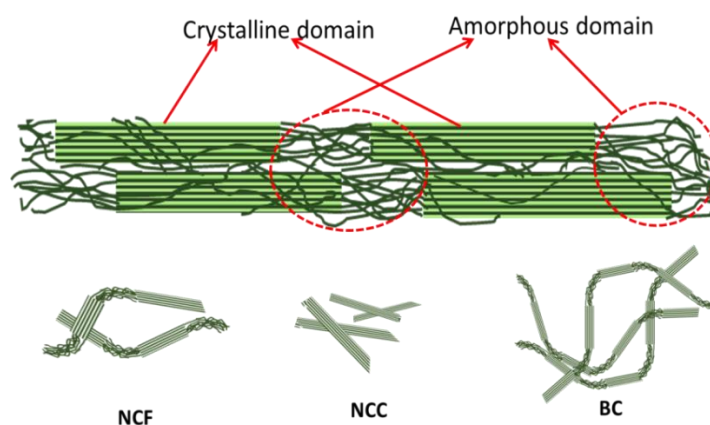


Figure 3. Schematic representation of typical semicrystalline nature of native cellulose with three variations of NC forms, *viz.* NCF, NCC and BC.

SCOPE OF NANOCELLULOSE

The ancient usage of cellulose was mainly limited in textiles and paper board industries where cotton cellulose and wood pulp had been utilized. As time progressed, cellulose has also been exploited as raw material for various commercial polysaccharides and many derivatives such as rayon, cellophane, etc. Later, by the discovery of NCs, it has been disclosed that when the lateral size of cellulose is reduced to the nanoscale, the material can replace many synthetic materials available in the market in terms of their strength, barrier properties, tunability and most importantly biocompatibility. Consequently, the nanoscopic features and properties of NCs have been exploited worldwide in a broad range of applications including, biomedicine, composites, nanoparticle synthesis, sensors, environmental monitoring, pollution control, etc. However, selecting the appropriate characteristics/properties of the cellulose material is vital for NC to be applied in different applications.

NANOCELLULOSIC HYDROGELS/AEROGELS AS FUNCTIONAL MATERIALS

The prime properties of cellulose microfibrils are its flexibility and propensity for entanglement owing to its high aspect ratio nanofibers and a greater extent of hydrogen bonding. An aqueous slurry/suspension of NCC/NCF/BC above a critical concentration can form three dimensional networks that hold water in their matrix called hydrogel. This gel upon removal of the solvent results in fine porous structured light-weight materials called aerogels. Hydrogels and aerogels of NCC/NCF/BC provide ideal platforms that could be materialized for various applications in environmental, energy and biomedical field. It should be taken into account that a regular oven drying leads to collapsed network structures by the capillary induced shrinkage of pores resulting in xerogel formation. Therefore, the removal of solvents from hydrogels often carried out by means of lyophilization or supercritical drying, which involves sublimation of water. Solvent exchange by less polar solvents followed by oven drying is an alternative to these two methods¹¹. All these approaches help to maintain the three-dimensional skeletal structures intact more or less, avoiding capillary effect to a great extent.

An NCF/BC hydrogel can find potential applications in biomedical fields as drug-delivering agent, wound dressing material, tissue regeneration scaffold, bioimplant, *etc*, whereas, the corresponding aerogels are widely employed where potent captivation of external nanomaterials and molecules, barrier properties, *etc* are necessitated. The barrier properties of NCF/BC aerogels include thermal and acoustic insulation. These properties are greatly affected by the density, pore structure, and alignments of NCF/BC microfibrils. It has been found that NCF has thermal conductivity ranges in 0.2–0.5 W m⁻¹ K⁻¹ whereas, the aerogel made out of the BC can have thermal conductivity as low as 0.031 W m⁻¹ K⁻¹ (almost similar to that of silica aerogel), indicating that they are highly suitable for thermal insulation applications. This is because of the inclusion of a large volume of air (sometimes >99%) within the porous channels.

Since NCF based aerogels can attain specific surface area exceeding 300 m²/g, it could be used as high class and green absorbents in environmental remediation applications. Additionally, the charged interfaces of NCFs are highly useful for making functional hydrogels such that they can accommodate a variety of functional nanomaterials. High aspect ratio NCFs can also impart flexibility and transparency to the fabricated device as per the need. NCF/BC could be employed either single-handed or in combination with various functional nanomaterials for the removal of many airborne and waterborne pollutants like heavy metals, organic dyes, oils, toxic gases, *etc*.

CONCLUSION

This chapter summarizes the basic concepts of nanocellulose materials and their implications as promising hydrogels/aerogels scaffolds in selected areas. Nanocellulose is known to be the future's greenest nanomaterial derived from almost inexhaustible bioresources, possesses unique combinations of properties, such as high entangling nature, excellent biocompatibility, flexibility, mechanical properties, etc. High aspect ratio NC microfibrils are known to form biocompatible and flexible organic hydrogels/aerogels capable of accommodating various functional entities, which would otherwise outperform most of the existing products. Owing to their high porosity and surface area along with tunable surface properties and barrier properties render NC/BC-based hydrogel/aerogel a potential candidate to be used in biomedical fields as well as in energy and environmental remediation sectors, as they could be tailored into biocompatible functional scaffolds for various implants, wound dressing, drug delivering agents, customized sorption or filtrating systems for different contaminants *etc.*

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ROLE OF ANTIOXIDANTS IN HUMAN LIFE

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There is no animal life without oxygen consumption and its conversion to water through mitochondrial electron transport of free radicals, in the course of oxidative phosphorylation and the production of ATP as the ultimate and immediate source of energy. Free radicals may also be formed as nitrogen, carbonyl, chlorine, sulfur and other reactive species. During oxidation electrons or hydrogen are transferred from one molecule to another, the latter serving as an antioxidant. Antioxidants, therefore, can stop the formation of free radicals and the chain reactions, which would otherwise result in cell damage or even death.

Oxidative stress in biological systems is a complex process that is characterized by an imbalance between the production of free radicals (FR) and the ability of the body to eliminate these reactive species through the use of endogenous and exogenous antioxidants. During the metabolic processes, a great variety of reactions take place, where the promoters are the reactive oxygen species (ROS), such as hydrogen peroxide (H_2O_2) and the superoxide radical anion ($\text{O}_2^{\cdot-}$), among others. A biological system in the presence of an excess of ROS can present different pathologies, from cardiovascular diseases to the promotion of cancer. Biological systems have antioxidant mechanisms to control damage of enzymatic and non enzymatic natures that allow ROS to be inactivated. The endogenous antioxidants are enzymes, such as superoxide dismutase (SOD), catalase (CAT), glutathione peroxidase, or non-enzymatic compounds, such as bilirubin and albumin. When an organism is exposed to a high concentration of ROS, the endogenous antioxidant system is compromised and, consequently, it fails to guarantee complete protection of the organism. To compensate this deficit of antioxidants, the body can use exogenous antioxidants supplied through food, nutritional supplements, or pharmaceuticals. Among the most important exogenous antioxidants are phenolic compounds carotenoids and vitamins C and some minerals such as selenium and zinc.

Free radicals are highly reactive compounds, they are chemical species associated with an odd or unpaired electron and can be formed when oxygen interacts with certain molecules. They are neutral, short lived, unstable and highly reactive to pair with the odd electron and finally achieve stable configuration. Once formed these highly reactive radicals can start a chain reaction they are capable of attacking the healthy cells of the body, causing them to lose their structure and function. Cells may function poorly or die if this occurs.

Reactive oxygen species [ROS], sometimes called as active oxygen species, are various forms of activated oxygen, which include free radicals such as superoxide ions ($\text{O}_2^{\cdot-}$) and hydroxyl radicals (OH) as well as non-free radical species such as hydrogen peroxide (H_2O_2). These ROS play an important role in degenerative or pathological processes, such as aging, cancers, coronary heart diseases, Alzheimer's disease, neurodegenerative disorders, atherosclerosis, cataracts and inflammations.

Living organisms have antioxidant defense systems that protect against oxidative damage by removal or repair of damaged molecules. The term 'antioxidant' refers to the activity of numerous vitamins, minerals and phytochemicals which provide protection against the damage caused by ROS.

An antioxidant is a molecule capable of slowing or preventing the oxidation of other molecules. Oxidation is a chemical reaction that transfers electrons from a substance to an oxidizing agent. Oxidation reactions can produce free radicals, which start chain reactions that damage cells. Antioxidants terminate these chain reactions by removing free radical intermediates and inhibit other oxidation reactions by being oxidized themselves.

Oxidative stress has been widely implicated in biomedical sciences during the last 20 years. It significantly participates in the pathophysiology of highly prevalent diseases such as diabetes, hypertension, atherosclerosis, acute renal failure, Alzheimer and Parkinson diseases among others. The metabolism of oxygen by cells generates potentially deleterious reactive oxygen species (ROS). Under normal conditions the rate and magnitude of oxidant formation is balanced by the rate of oxidant elimination. Antioxidants interfere with the oxidative processes by scavenging free radicals, chelating free catalytic metals and by acting as electron donors. The natural antioxidant mechanisms may be insufficient in variety of conditions and hence dietary intake of antioxidant compounds are important.

Antioxidant compounds in food play an important role as a health protecting factor. Plant sourced food antioxidants like vitamin C, vitamin E, carotenes, phenolic acids, phytate and phytoestrogens have been recognized as having the potential to reduce disease risk. Most of the antioxidant compounds in a typical diet are derived from plant sources and belong to various classes of compounds with a wide variety of physical and chemical properties. Some compounds such as gallates which has strong antioxidant activity, while others such as the mono-phenols are weak antioxidants. The main characteristic of an antioxidant is its ability to trap free radicals.

Most plant-derived foods have a range of antioxidant compounds which include vitamin C (at lower exposures), vitamin E (tocopherols and tocotrienols), polyphenols, carotenoids and ubiquinol. Flavonoids promote antioxidant activity, cellular health and normal tissue growth and renewal throughout the body. They also work with vitamin C to reduce oxidative stress for the water based portion of the cell and may slow down some of the effects of aging. There are more than 4,000 unique flavonoids and they are most effective when several types are consumed together. Food sources include: cranberries, kale, beets, berries, red and black grapes, oranges, lemons, grapefruits, and green tea.

Antioxidant capacity is required both extra and intracellular (in cytosol, nucleus and mitochondria) for the homeostasis of oxidant status. Physical activity increases the oxidant load, and, if regular, progressively increases the body's ability to respond to such a load. Pro-oxidant foods are principally those with excessive metals such as manganese, iron, or copper or when vitamin C (ascorbic acid) exceeds that usually obtainable from food by way of supplements.

Antioxidants are often added to foods to prevent the radical chain reactions of oxidation, and they act by inhibiting the initiation and propagation step leading to the termination of the reaction and delay the oxidation process. Due to safety concerns of synthetic compounds, food industries have focused on finding natural antioxidants to replace synthetic compounds. In addition, there is growing trend in consumer preferences for natural antioxidants, all of which has given more impetus to explore natural sources of antioxidants.

Synthetic antioxidant like butylated hydroxyl toluene (BHT), butylated hydroxyl anisole (BHA), propylgallate (PG) and *tert*-butyl-hydroquinone (TBHQ) are known to ameliorate oxidative damages but they have been restricted due to their carcinogenic and harmful effect on the lungs and liver. Therefore, investigations of antioxidants are focused on naturally occurring substances, especially plant phytochemicals. There are two major groups of antioxidants in living cells: enzymatic antioxidants and non-enzymatic antioxidants. These groups are divided into several subgroups. The enzymatic antioxidants are divided into primary and secondary enzymatic defenses.

The primary defense is composed of three important enzymes that prevent the formation of and neutralize free radicals: glutathione peroxidase, which donates two electrons to reduce peroxides by forming selenols and also eliminates peroxides as potential substrates for the Fenton reaction; catalase, which turns hydrogen peroxide into water and molecular oxygen—one of the most important and efficient antioxidants known today, when just one molecule of catalase converts 6 billion molecules of hydrogen peroxide; and lastly, superoxide dismutase, which converts superoxide anions into hydrogen peroxide as a substrate for subsequent catalase action.

The secondary enzymatic defense includes glutathione reductase and glucose-6-phosphate dehydrogenase. Glutathione reductase reduces glutathione (antioxidant) from its oxidized to its reduced form, and by this recycling, to continue neutralizing more free radicals. Glucose-6-phosphate regenerates NADPH, which creates a reducing environment. These two enzymes support the primary enzymatic defense antioxidants and do not neutralize free radicals directly.

HEALTH BENEFITS OF ANTIOXIDANTS

The human body has a complex system of natural enzymatic and non-enzymatic antioxidant defenses which counteract the harmful effects of free radicals and other oxidants. Protection against free radicals can be enhanced by ample intakes of dietary antioxidants, of which the best studied are vitamin E, vitamin C and carotenoids. Substantial evidence indicates that foods containing antioxidants and possibly in particular the antioxidant nutrients may be of major importance in disease prevention. Efforts should be made to ensure optimum intakes of foods containing these important molecules. There is a need for improvement in the quality of the diet, especially with respect to increased consumption of fruits and vegetables. However, other strategies, including optimization of food processing, selective fortification of foods and the use of safe nutritional supplements, may also need to be considered. All three of the major antioxidant nutrients — vitamin E, vitamin C and β -carotene — are safe even at relatively high levels of intake. There is, however, a growing consensus among scientists that a combination of antioxidants, rather than single entities, may be more effective over the long term.

Cancer

Cancer is the end point of a multistep process involving a sequence of events that occur over a period of years or even decades. Antioxidant nutrients and the foods that contain them may have important protective effects in the prevention of human cancer. The evidence for a beneficial effect of fruits and vegetables is over-whelming. The evidence for protective effects from individual antioxidant nutrients is less definitive, and therefore other constituents of a diet may also play an important role.

DNA damage is considered to be one of the most important contributors to cancer. Much of this damage is oxidative in nature. A marker of mutagenic DNA damage would be

useful in the estimation of cancer risk of various populations and in monitoring the effects of chemoprevention. Much of this damage is oxidative in nature. If a cell containing damaged DNA divides before its DNA can be repaired, the result is a permanent genetic alteration, the first step in carcinogenesis. Cells that divide rapidly are more susceptible to carcinogenesis than slowly dividing cells because there is less opportunity for DNA repair before cell division.

Oxidants and antioxidants may also play a role in the later stages of cancer development. There is increasing evidence that oxidative processes contribute to the promotion stage of carcinogenesis, although the mechanisms for this are not well understood. Antioxidants may be able to cause the regression of premalignant lesions or inhibit their development into cancer. Preliminary studies have indicated that some antioxidants, particularly β -carotene, may be of benefit in the treatment of precancerous conditions such as oral leukoplakia (which may be a precursor of oral cancer). Some antioxidant nutrients may protect against cancer through mechanisms other than their antioxidant properties. For example, carotenoids may both enhance immune function and increase gap functional communication (a type of interaction between cells that inhibits cell proliferation); both of these actions may be relevant to cancer prevention.

Cardiovascular disease

Oxidation may play a role in cardiovascular disease in two ways, one involving the long-term development of atherosclerosis and the other involving the immediate damage that occurs during a heart attack or stroke. Antioxidants may help counteract both of these processes.

The role of free radicals in heart attacks has been assessed in experimental model systems. Free radicals have been found to accumulate in isolated heart muscle that has been subjected to a temporary interruption of blood flow. In some experimental models, treatments that inhibit the accumulation of free radicals have been shown to reduce the severity of damage to the heart muscle. In one human study, pretreatment with vitamin C was apparently of benefit to patients who underwent long periods of cardiac arrest during cardiopulmonary bypass surgery. The release of enzymes associated with ischemia was strikingly decreased in those patients who received vitamin C, indicating a reduction in cell damage. High intakes of antioxidants with reduced risks of cardiovascular diseases. The evidence is strongest for vitamin E, limited but promising for β -carotene, and inconsistent for vitamin C.

Eye diseases

Age-related diseases of the eye are major health problems around the world. In technologically developed countries, the treatment of cataracts is one of the largest contributors to total health care costs for the elderly. In less developed countries, where treatment is often unavailable, cataracts are a major cause of blindness in older adults. World-wide, approximately 50 million people are blind from cataracts.

Cataracts occur when transparent material in the lens of the eye becomes opaque. Much of the material in the lens consists of extremely long-lived proteins, which can become damaged over the decades of a human lifetime. Since there is no direct blood supply to the lens, nutrients enter and waste products are removed by a simple diffusion process which is slow and inefficient. Oxidation, induced primarily by exposure to light, is believed to be a major cause of damage to the proteins of the lens. When these proteins become oxidized, they clump together and precipitate, causing portions of the lens to become cloudy.

The eye has defense systems which protect the lens from oxidative damage. Antioxidants and antioxidant enzymes inactivate harmful free radicals and proteases (enzymes which break down proteins) selectively remove damaged proteins from the lens. However, these defense systems cannot always keep pace with oxidative damage. As a result, oxidized proteins may accumulate. As people age, the defense systems grow less effective, and damage to lens proteins may become irreversible. High intakes or blood levels of antioxidant nutrients will reduce the rates of cataract. All three of the major dietary antioxidants — vitamin C, vitamin E and carotenoids — have been associated with decreased cataract risk.

Age-related macular degeneration

Excessive exposure to light and the resulting production of oxidants contribute to the causation of age-related maculopathy. In particular, exposure to blue light has been implicated in this disorder. If blue light is involved, carotenoids might be protective, since they can absorb blue light.

The vitamin A in foods actually consists of carotenoids precursors of the vitamin rather than preformed vitamin A (retinol). Age-related maculopathy found markedly reduced risks in individuals with high blood carotenoid levels. Significant associations were detected for the sum of all carotenoids and for four of five individual carotenoids (β -carotene, α -carotene, cryptoxanthin and lutein/zeaxanthin, but not lycopene). Vitamin C and vitamin E did not show significant effects.

Neurological disorders

Oxidation may play a role in the causation of several disorders of the brain and nervous system. Therefore, it has been hypothesized that antioxidants might be helpful in ameliorating the symptoms or in slowing the progression of some neurological disorders. Studies have shown beneficial effects of vitamin E supplementation in decreasing the severity of tardive dyskinesia; others have not found an effect. Tardive dyskinesia is a disorder involving involuntary movement. It occurs as a side effect of long-term treatment with certain antipsychotic drugs.

Sperm damage, birth defects and childhood cancer

The children of fathers who smoke cigarettes have increased rates of congenital malformations and childhood cancer. These problems may be related, at least in part, to increased oxidative damage to sperm cells caused by oxidants in cigarette smoke. Cigarette smoking is associated with reduced sperm count and poor sperm quality; it is also associated with decreased blood vitamin C levels. Vitamin C supplementation has been shown to improve sperm quality in heavy smokers. Ample intakes of vitamin C have also been shown to reduce oxidative damage to sperm DNA. Further studies are needed to determine whether improved antioxidant status, particularly with respect to vitamin C, is of benefit in reducing infertility and germ-line mutations in men who smoke cigarettes or who are exposed to oxidative stress from other causes.

Exercise-induced oxidative stress

Because exercise leads to increased oxygen consumption, it causes an increase in the production of oxygen-initiated free radicals. Some studies have reported that antioxidant supplementation reduces evidence of exercise-induced muscle damage. Antioxidants may also play a role in reducing muscle soreness after overexertion. However, it is unclear whether antioxidants can directly enhance physical performance.

Inflammatory disorders

Free radicals and oxidative stress may play a role in inflammatory diseases. Rheumatoid arthritis is one example. The products of free radical reactions have been detected in the blood and joints of patients with this disease. Other lines of evidence also suggest the involvement of oxidative stress in rheumatoid arthritis and in other inflammatory diseases such as glomerulonephritis.

Decrease in immune function

Several aspects of immune function show a marked decline with increasing age. Preliminary studies in elderly people have indicated that this decline can be partly offset by dietary antioxidant supplementation. The age-associated decrease in cell-mediated immunity may be due to a decreased level of small-molecular-weight antioxidants and decreased activity of antioxidant enzymes.

Rheumatoid arthritis

Rheumatoid arthritis is an autoimmune disease characterized by chronic inflammation of the joints and tissues around the joints with infiltration of macrophages and activated T cells. The pathogenesis of this disease is due to the generation of ROS and RNS at the site of inflammation. Oxidative damage and inflammation in various rheumatic diseases were proved by increased levels of isoprostanes and prostaglandins in serum and synovial fluid compared to controls.

Antioxidants are absolutely critical for maintaining optimal cellular and systemic health and well-being. Naturally there is a dynamic balance between the amount of free radicals produced in the body and antioxidants to scavenge or quench them to protect the body against deleterious effects. The amount of antioxidant principles present under normal physiological conditions may be insufficient to neutralize free radicals generated. Therefore, it is obvious to enrich our diet with antioxidants to protect against harmful diseases. Hence there has been an increased interest in the food industry and in preventive medicine in the development of "Natural antioxidants" from plant materials. The possible toxicity of synthetic antioxidants has resulted in decreased use of these compounds in foods for human consumption. As a consequence of this and due to the appeal of natural products to consumers, numerous studies have been carried out in order to identify naturally occurring compounds which possess antioxidant activities such as phenolic phytochemicals.

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WATER POLLUTION AS A GLOBAL ENVIRONMENTAL PROBLEM AND THE REMOVAL OF AMMONIA FROM DRINKING WATER

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INTRODUCTION

Earth, the most beautiful planet in solar system is entirely different and extremely peculiar from all other spheres in the universe because of the magical substances present in the earth known as air and water. Water is a very essential element and is an extremely important material for the existence of any living organism. Life on earth is never expected without the availability of water. We know that two third of earth's surface is covered by water. Actually 97.3% of the total water on earth is in oceans and seas as saline water. Out of the rest, 2% are in the mountains and glaciers of the polar regions like Artic and Antarctic continents. Only 0.6% is potable water or fresh water and is concentrated at rivers and lakes as surface water in underground aquifers as ground water. Hence only a small portion of this can be attained for all living things, which lives on land, including human being. Total quantity of water on earth remains constant in all circumstances. The earth is maintaining it by continuously purifying the water sources through a process known as hydrological cycle. In hydrological cycle, water undergo an endless movement from the soil to the atmosphere. This continuous movement from soil, water bodies and again to atmosphere and vice versa is happening by the help of two natural processes known as evaporation and condensation.

Water available in the nature is distributed in different forms. They are mainly classified as rain water, surface water and ground water. Besides this, water is also distributed as snow and moisture.

RAIN WATER

Rain water is a very important source of water to the inhabitants of the earth, and also plays a major role in ensuring the water cycle is complete. It is the purest form of water available in nature. Mostly it is free from pollution with a clear, bright and sparkling appearance. Rain water is chemically very soft and it contains only traces of chemicals as dissolved solids. The total dissolved solids in rain water are approximately 0.005%. Rainwater fills streams, rivers, lakes and that ultimately carry the water back to the sea.

SURFACE WATER

Surface water is nothing but the water available on the surface of the earth. The water found in stream, river, lake, wetland and oceans are examples of surface water. It is easily decreased through evaporation to atmosphere and seepage into the underground where it becomes ground-water. One of the main sources of water for human use is surface water. Except drinking and public uses, surface water is used for irrigation, industrial purposes,

travelling, production of electricity, thermo electric and nuclear power stations etc. It is used by plants for transpiration and by other animals and creatures for their vital necessities. It also continuously discharges to the oceans and seas where it becomes saline. About 77% of the freshwater used in India is from surface-water sources and the rest of 23% is from ground water. Among the surface water sources, most important drinking water sources are rivers.

GROUND WATER

Ground water is the water laid in underground layers and aquifers. The surface water percolated through the soil and collected in underground cavities is known as ground water. Ground water comprises the vast majority of fresh water and is the primary and very important source for drinking water for most of the human population. Ground water is more chemically contaminated than surface water. This is because, when percolated through the soil, there are chances of many chemical compounds to dissolve in it. But it has an advantage of free from pathogenic agents.

India is blessed with a large number of rivers as like a network. Hence India is comparatively rich in surface water resources and gifted with numerous lakes. Our country is also blessed with heavy snow mountain, Himalaya. About 90% of its water resources are used for agriculture and 3% for domestic use. At global level this is about 70% for agriculture and 5% for domestic use. But in industrialised countries, up to 25% is used for industrial purposes where in India only 7% is used for industrial use.

Kerala is known as God's own country because of its abundant natural resources especially water. The state receives a tremendous amount of rain water every year of about a huge value of 3000-3300mm of rain. There are 44 rivers and 34 backwaters mostly in the form of lakes and ocean inlets and others are fresh water lakes. Besides these, Kerala is also blessed with numerous streams, about 18600 of ponds and over 70 lakhs dug wells. Kerala has one of the most dug well densities in the world.

Water is commonly known as universal solvent; this is because it consists of exceptional quality of dissolving a number of substances without changing their chemical nature. Therefore, water plays a very important role in all living organisms. All water bodies including oceans and seas are utilizing by a huge number of people, animals, birds and other creatures for their biological activities. We are using water for our needs such as drinking, cooking, cleaning, washing, farming and irrigation. Main component of the human body is water and is about 60-68%. The mean daily intake of water by a man is estimated to be 3.1% of his body weight. If about 2% of water content is lost from our body, then a human may fall into unconscious state and may lead to death.



Edible water must not contain substances that cause adverse effects, but at the same time, it should be aesthetically acceptable to the consumer. Such water is termed as fresh water, which must be free from bacteriological and chemical contamination and promote the health of the community. Contaminated water is associated with health risks and leads to the spread of diseases such as dysentery, cholera, typhoid, diarrhoea and fluorosis, blue baby

syndrome and so on. Access to safe drinking water is a prerequisite to poverty reduction and prevention of the spread of water-borne and sanitation related diseases. Naturally, when contaminants enter into the water bodies, they can absorb the contaminants without affecting its quality. But when the amount of pollutants becomes high or the pollution load is exceeded than the natural regenerative capacity of a water resource, then the water body is said to be polluted.

WATER POLLUTION

One of the most serious issues in the modern world is water pollution. It is one of the main side effects of the sudden and great development of human race. When the population increases, human needs also increases up to a maximum. The increase of human needs might cause to live as crowded and it made towns and cities. For safety and convenience, people from villages accustomed to migrate into the town. This increases urbanisation and due to this lot of peoples forced to live in a small area. With the scientific development and living amenities, the daily demand and per head consumption are increasing day by day and this also increases the production of polluted water as well as it might pollute the water sources. With the population hike, it was needed to widen agriculture as well as agricultural production also. Due to this the spread of chemicals such as fertilizers, pesticides and insecticides etc. are uncontrollable and this increases the pollution of water as well as earth up to a maximum. Some of the important reasons for water pollution are sudden hike in population, urbanization and change of living style, industrialization, uncontrolled use of water and unscientific methods in agriculture.

Water pollution can be classified as two types on basis of the sources of pollution. They are point sources and non-point sources. Point sources are clearly discharging of pollutants into water sources. They include factories, Agricultural runoff, untreated waste water, water and waste water plants, industrial effluents and municipal wastes etc. Non-point sources include household wastes, agricultural runoff such as sediments, fertilizers and chemicals such as pesticides and insecticides, wastes from farm houses and wastes from mining sites. Landfills and construction sites are also considered as a non-point source of pollution.

Water pollutants include both organic and inorganic factors. Organic factors may be the volatile organic compounds, fuels, waste from trees, plants etc. Inorganic factors include ammonia, chemical wastes from different industries etc. Agricultural wastes such as pesticides, fungicides, fertilizers, human and animal faeces, seepage from pit latrines and septic tanks, refuse dump, industrial, domestic and all municipal wastes released into water bodies are often responsible for water contamination.

Pollutants may cause obvious (colour change, taste difference or objectionable smell) or asymptomatic issues on the quality of water. When rain water is oozing through the soil, many chemical contaminants may miscible with the water and hence the ground water sources were also contaminated. The depth of the sources become more polluted due to the chances of chemical miscibility is more when increases the distance of travelling of the water. The pathogenic bacteria, virus, protozoan's, amoeba, which are causes dangerous diseases like cholera, hepatitis, polio etc are entered into the water sources through pollution.

SOURCES OF POLLUTION

There are various sources like faeces of humans, animals, birds etc. household solid and liquid wastes, wastes from hospitals and factories, waste water from cattle field and farmhouses, salt water intrusion from sea, dissolved salts, minerals etc. Water pollution may

cause a change in the physical, chemical and biological properties of natural water due to contamination with any undesirable substances. So, we can determine the extent of water pollution by measuring physical chemical and biological parameters of water.

WATER QUALITY PARAMETERS AND LIMITS

Introducing the water quality monitoring method and the necessarily arrangements impelled by the scientific world is obviously emerging from the continuous issues affected on the water quality. As per the quality aspects of water, it may be described as follow

1. Physical: An obvious change in the colour, taste or odour due to the pollution
2. Chemical: Exuberance of the salts, minerals and other chemical contaminants in the water causes chemical issues. For example, chloride, fluoride, iron, arsenic *etc.*
3. Biological and bacteriological: This is due to the presence of microbial such as bacteria.

Most of the people depend the open wells or shallow wells and each house has at least one well. These sources are often surrounded by so many pits like soak pit, leach pit, pit latrines and septic tanks *etc.* and increases the chances for contamination. The contaminant water may leach from the pits for collecting kitchen waste water or bathroom waste water or from soak pit used for collecting septic waste. In rainy seasons there will be excess quantity of water in all sources and hence less chemical quality problems were found. But in summer season the quantity of water in most of the sources become less and so most of the sources gets polluted and thus cannot be used for drinking purposes. Most of the drinking water sources were found to be below the standards specified by the Bureau of Indian Standards. These alarming results stress the need and importance of regular water quality surveillance in water quality management.

In India, commonly we follow IS 10500, 2012 for drinking water quality parameter. Two limits namely desirable limit and permissible limit are to be measured. The desirable limit means, the quality parameters are very good within the limit. When the quality parameter exceeds the limit and we have no other water sources to depend, then only the people have to use quality parameters within the permissible limit. When the permissible limit is exceeded, the source has to be rejected or to be used only after done proper treatment processes.

IMPORTANT WATER QUALITY ISSUES FOUND IN KERALA

One of the most important problems found in the open well water sources are of low pH. Normally when pH decreases the acidity of the water will increase. About 70 % of water sources, especially open wells were affected with low pH. It may be due to the presence of carbon dioxide, which miscible from the surface soil in water.

Excess turbidity is one of the quality issues found in Kerala. The torrent of heavy water in rainy season to be mixed with more soil, clay and other suspended particles in water makes it more turbid. But in summer season the presence of iron, algae and other dust particles makes the water turbid. Turbidity gives the water as unpalatable in appearance and to set against the disinfection.

Iron contamination in drinking water is an egregious and effusive water quality problem found in water. An unpalatable taste of iron, increasing turbidity when water in contact with air, leaving stains on utensils, cloths, tiles and closets and an oily appearance on the surface of water sources are some of the qualities problem accompanied with the presence of excess iron contamination in water bodies.

Another notable issue about water quality is the presence of organic pollutants. It is not an exceptional quality problem in Kerala, because of its high population density. It is due to the presence of pollutants which are reached out from houses, hospitals, markets, industries, agricultural field etc. Ammonia as well as nitrate contaminations is found as new emerging issues in water sources especially in drinking water sources, mostly accompanied with organic pollution.

Table 1: Water Quality Parameters as per IS 10500:2012

<i>Sl.No</i>	<i>Parameters</i>	<i>Unit</i>	<i>Desirable Limit</i>	<i>Permissible Limit</i>
1	Turbidity	NTU	1	5
2	Taste, Colour, Odour		Unobjectionable	Unobjectionable
3	Temperature	⁰ C		
4	pH		6.5-8.5	6.5-8.5
5	Total Dissolved Solids (TDS)	mg/L	500	2000
6	Acidity	mg/L		
7	Alkalinity	mg/L	200	600
8	Total Hardness	mg/L	200	600
9	Calcium as Ca ²⁺	mg/L	75	200
10	Magnesium as Mg ²⁺	mg/L	30	100
11	Chloride as Cl ⁻	mg/L	250	1000
12	Fluoride as F ⁻	mg/L	1	1.5
13	Iron as Fe ²⁺	mg/L	0.3	No Relaxation
14	Nitrate as NO ₃ ⁻	mg/L	45	No Relaxation
15	Sulphate as SO ₄ ⁻	mg/L	200	400
16	Ammonia as NH ₃	mg/L	0.5	No Relaxation

AMMONIA IN DRINKING WATER

Ammonia is not a regular or naturally occurring substance in fresh water or unpolluted water. But when water is mixed or contaminated with sewage water or organic wastes like animal waste and other decomposed organic matters, ammonia may be present in excess amount. Ammonia also can enter with the water bodies through municipal effluent discharges, direct discharge of animal excreta, by means of the activity of nitrogen fixation bacteria, run off from agricultural lands and from industries. Ammonia is excreted by fish as a nitrogenous waste product which is the by-product of protein metabolism. In most of the organic and inorganic fertilizers, nitrogen disposed from plants, synthetic glass cleaners, floor and toilet cleaners are other sources of ammonia.

According to WHO, natural level of ammonia in drinking water sources should be below 0.2 mg/L. Presence of excess amount of ammonia in drinking water may indicate the presence of faecal contamination. Ammonia contamination in drinking water sources may cause a change in taste. Presence of ammonia decreases the efficiency of disinfection when using chlorine as the disinfectant are another important problem associated with high.

Ammonia contamination in water will affect adversely for dialysis patients. Its toxicity varies with the pH of the water and it became toxic for fresh water fishes.

USEPA (US Environmental Protection Agency) has established the environmental limit of ammonia in surface water is in the range from 0.25 to 32.5 mg/L. In India, the Bureau of Indian Standards (BIS) have recommended the desirable as well as the permissible limit of ammonia in drinking water is limited to 0.5mg/L. European countries also adopted the ammonia concentration above 0.5 mg/L as the cause for rejection of water for drinking. As per the advice of United States Environmental Protection Agency, the maximum level of ammonia consumed in a lifetime should not be more than 30mg/L. Excessive amount of ammonia in drinking water are associated with many potential hazards.

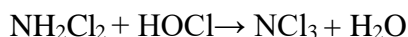
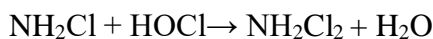
1. The presence of excess amount of ammonia may lead to the growth of autotrophic bacteria. This certainly stimulates the undesirable bacterial growth in water bodies which contain both non-pathogenic as well as pathogenic.
2. The autotrophic bacteria associated with excess ammonia convert ammonia into nitrate as well as nitrite. A high concentration of nitrate and nitrite causes health hazards. The excess amount of nitrate and nitrite in drinking water may cause blue baby syndrome or methemoglobinemia in infants and foetus. It may also increase a chance of producing nitrosamine, a carcinogenic compound.
3. Even if the ammonia with low concentration in water as NH_3 is toxic to fresh water fishes.
4. Excess of ammonia contamination in water bodies enhances the growth of algae as well as weeds and this may cause to algal blooming and DO depletion and ultimately it leads to eutrophication. Eutrophication will demolish completely the water body forever.
5. According to the Office of the Environmental Public Health, low concentration ammonia has a toxic effect to the aquatic creatures and fresh water fishes, but it does not have a significant effect on higher animals like human being. But they emphasize that long term conception of ammonia more than 1 mg/L through drinking water may damage the internal organs of human being.

TECHNOLOGIES FOR REMOVAL OF AMMONIA

1. Ion exchange method using zeolite: Ammonia can be removed from water by ion exchange method. Zeolite is used as the ion exchange resin and it can be easily regenerated by common salt. When using sodium alumina silicate zeolite, 1ppm to 20ppm of ammonia can be removed with a moderate flow rate. This method is not applicable in residential purposes. But this method is used in large scale for public and private water supply schemes more effectively and economically. Natural zeolites like clinoptilolite is also used for as ion exchange resin. High hardness of water will have an adverse effect in the removal of ammonia in ion exchange resin method. This is due to the simultaneous affinity of calcium, magnesium and the ammonium ion with the zeolite. Hence this method is more effective in soft waters or water has low hardness. Degasification by aeration or adopting any other method for degasification is also is a good method for removing ammonia.

2. Break point chlorination: Break point chlorination is a method of removing ammonia using chlorine. This is a very common method and has been applied for decades. In this method, chlorine is applied as bleaching powder or chlorine liquid or gas form. Firstly, the chlorine is reacted with water to form hypochlorous and it will react with the ammonia present in water and then undergo the following reactions.



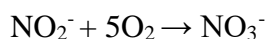


When the protonated ammonia is reacted with the acid, firstly monochloramine is produced. Monochloramine is then reacted with hypochlorous acid to form dichloro and then trichloramine is formed. When the concentration of ammonia becomes less in water, then the free chlorine is appeared as residual chlorine. Trichloramine, formed in the third stage is highly unstable and so it is immediately decomposing to form nitrogen gas. The by-products of organo-chlorines or THM etc. often appear as the by-product of chlorination, under these conditions will rise its unwanted presence. The formed chloramines give an unpleasant odour to treated water.

3. Biological method for ammonia removal: The biological removal is a nitrification method. In this method chemoautotrophic bacteria are used as the nitrifying bacteria and uses both carbon dioxide and ammonia present in water. Carbon dioxide is used as the carbon source and ammonia is for energy source. This process takes place in two steps. In the first step, the bacteria oxidise the protonated ammonia in water to nitrite



In the second step the nitrite oxidizing bacteria oxidises nitrite to nitrate.



The above reaction is carried out in the presence of dissolved oxygen and at favourable temperature. So, this process causes a decrease in the dissolve oxygen level in water and enhances the growth of nitrifying bacteria in water.

4. Adsorption by charcoal: The removal of ammonia using different charcoals is also reported and found to be highly effective. Charcoal is a good adsorbent and is very commonly used for water filtering. The commonly used charcoals are wood charcoal, activated charcoal, charcoal from rice husk and animal charcoal. One of the reliable and effective charcoals for the removal of excess ammonia is the charcoal available by the charring of rise husk. Charcoal is widely used in water filters for removing dissolved gases in water. Wood charcoal and activated charcoal are mainly used in water filters but the rate of adsorption is very low. From our study, it is established that the adsorption capacity of rise husk charcoal against ammonia is very high and is up to about 97%. Some other methods like are aeration followed by filtration, pyrolusite media filtration, membrane filtration and stabilization and sequestering.

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SCAFFOLDS FOR THE APPLICATION OF PHOSPHORESCENT ORGANIC LIGHT-EMITTING DIODE

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INTRODUCTION

Organic light-emitting diodes (OLEDs) have attracted unprecedented attentions due to their widespread applications in lighting and displays¹. OLEDs are electronic devices, which function on the principle of electroluminescence. They consist of thin film of organic materials sandwiched between two electrodes, namely anode and cathode. When electric potential is applied between electrodes, light is emitted. Interestingly, OLED-based displays are endowed with many superior features like: light weight, low-power consumption, self-emitting property, high luminous efficiency, full color tunability, wide viewing angle, high contrast ratio and flexibility. These unique features of OLEDs have rendered them potential rival of contemporary LCD technology. This is evident from the burgeoning growth in the market value of OLED displays, which is expected to reach millions of USD by 2025. Not restricted to displays, OLEDs are also potential candidates in the area of solid-state lighting due their appealing power efficiency and aesthetics. This has led OLED-based lighting to slowly replace the market of CFL tubes and incandescent bulbs.

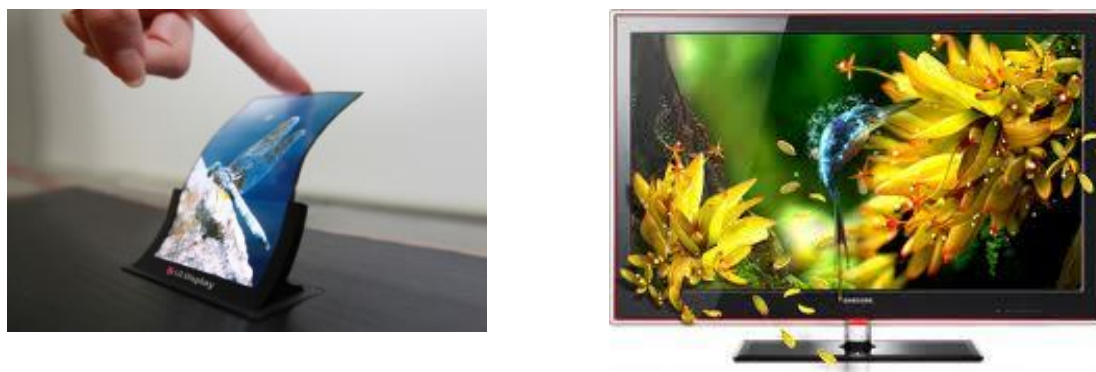


Figure 1. Thin and flexible OLED displays endowed with wide viewing angle.

HISTORY

Electroluminescence was first observed by Destriau *et al* in 1936. In 1950s Andre Bernanose and his coworkers at Nancy University in France first observed electroluminescence from an organic material, when they applied high voltage alternating current across acridine orange deposited on cellulose or cellophane thin film. Similarly, electroluminescence from single crystal of anthracene was observed by Martin pope and

coworkers from New York University in 1963. These studies created fundamental understanding of various physical aspects of electroluminescence, like: charge injection, charge mobility, exciton formation and light emission. Nevertheless, the technology remained incipient due to associated difficulty with attaining high working voltage, growing single crystals and achieving reliable electrical contacts. The renaissance in the field was brought by Tang and Van Slyke from Kodak in the year 1987, when they fabricated first diode employing thin film of vapor deposited material and coined the term OLED for this diode. Notably, the diode fabricated by Tang and Van Slyke had three components, hole-transport layer, emissive layer and electron-transport layer.

DEVICE ARCHITECTURE

OLEDs are semiconductor devices of ~100 to 500 nanometers thickness. They consist of thin layer of organic materials sandwiched between two electrodes. The main components of device functioning on the principle of electrofluorescence are: anode, cathode, hole-transport layer, electron-transport layer and emissive layer (**Figure 2**). When forward bias is applied, holes from the anode are injected into the HOMO of the hole-transport layer and electrons from the cathode are injected in to the LUMO of the electron-transport layer. In the presence of forward bias, holes and electrons move towards each other and combine in the emissive layer to generate excitons. These excitons are species in the excited energy state and undergo radiative decay leading to electroluminescence. Importantly, balanced hole-electron injection and transport is crucial for attaining high efficiency. This has led to the evolution of multi-layer configuration over the year for attaining high device efficiency (**Figure 3**). The major components for electrofluorescent device are listed below.

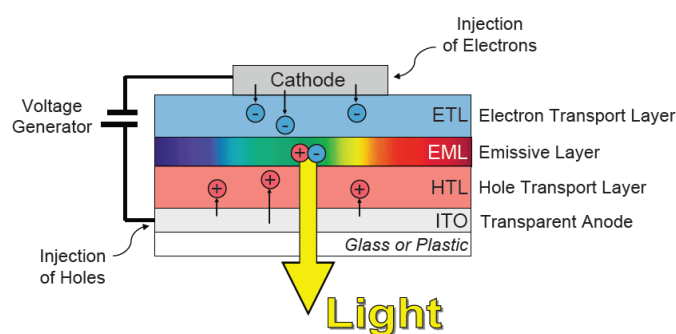


Figure 2. OLED device architecture containing anode, cathode, hole-transport, electron-transport and emissive layer.

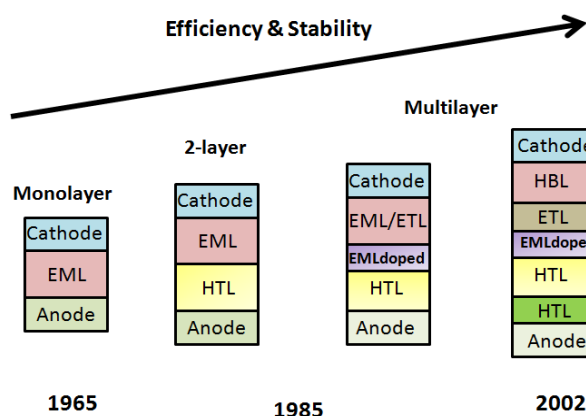


Figure 3. Evolution of multi-layer OLED device architecture over the years.

Anode

Conventionally, OLEDs are fabricated on a substrate coated with a transparent conducting electrode, which can emit light through it. Transparent conducting oxide [TCO] such as Indium tin oxide [ITO] is commonly used anode for OLEDs. ITO has high work function (have more positive electrical potential) and is transparent. Importantly, work function of ITO falls in the range of 4.5-5.0 eV, which facilitates hole-injection into the HOMO of hole-transport layer. Beside ITO, graphene is another commonly explored transparent anode employed for OLED displays.

Cathode

Cathode is composed of metals like: barium, calcium and aluminium. These metals have low work function of 3-4 eV, which facilitates electron injection from cathode into LUMO of the electron transport layer.

Conducting Layers

Physical processes involved during operation of OLEDs are: charge injection, charge transportation, exciton formation and light emission. The organic layers are electrically conducting due to the presence of conjugated π electrons and transport charges by hopping layers⁶.

Hole transport materials: Hole transport materials (HTMs) are derivatives of electron rich species, like: triarylamine, diphenylamine, carbazole, *etc.* Requisites for a material to be useful as HTM are: good hole mobility, low lying HOMO energy, amorphous property, high glass transition temperature (T_g) and thermal decomposition temperature (T_d). These features allow them to form thermally and morphologically stable films without phase separation caused by crystallization. Low lying HOMO level of HTMs ensures low energy barrier for injection of holes from anode. Most commonly employed HTMs are: 4,4'-bis[N-(p-tolyl)-N-phenylamino]biphenyl(TPD), N,N'-Di(1-naphthyl)-N,N'-diphenylbenzidine(NPB), 4,4',4''-tris(N-carbazolyl)triphenylamine(TCTA) and 1-Bis[4-[N,N-di(4-tolyl)amino]phenyl]-cyclohexane(TAPC),^{7,8,9,10} (Chart 1).

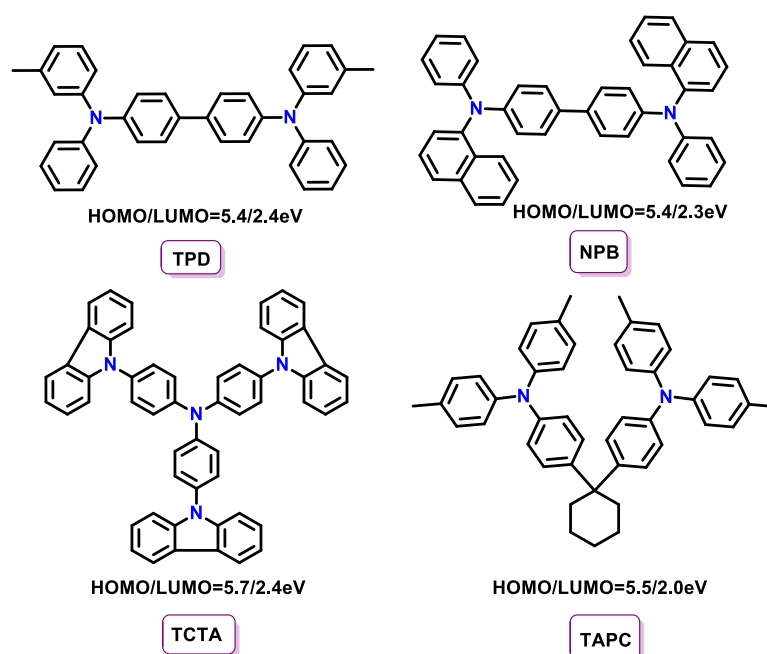


Chart 1: Structures of commonly employed HTMs.

Electron transport materials: Electron transport materials contain electron withdrawing groups in their molecular structure to facilitate electron injection and transport. Similar to hole-transport materials, these materials should possess good electron mobility, deep LUMO level, amorphous property, high thermal stability. The most commonly employed electron transport materials are: Alq₃ (tris(8-hydroxyquinoline)aluminium), TPBI (1,3,5-tris(N-phenylbenzimidazol-2-yl)benzene), BCP(4,4'-bis(9-carbazolyl)biphenyl) and PBD(2-(4-tert-Butylphenyl)-5-(4-biphenyl)-1,3,4-oxadiazole)^{11,12} (**Chart 2**).

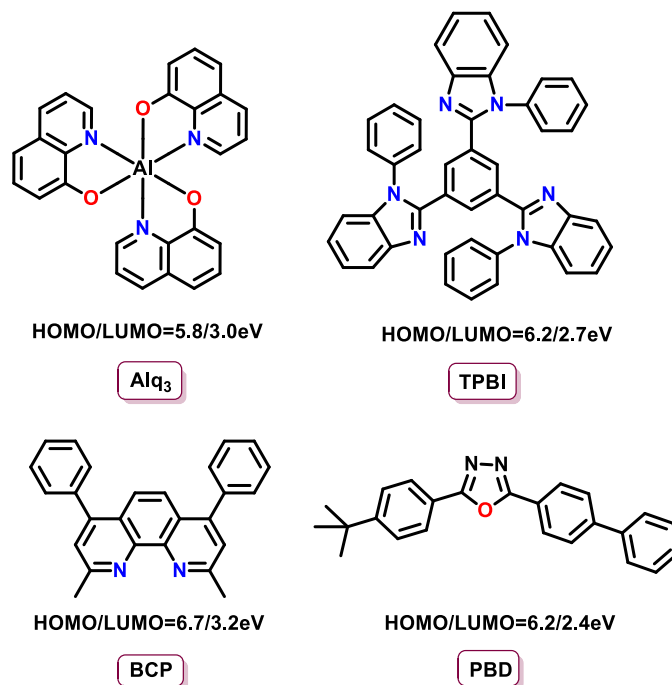


Chart 2: Structures of commonly employed ETMs.

Emissive materials: As discussed at the outset, hole and electrons drift towards each other in the presence of applied potential and combine in the emissive layer to form excitons in an OLED device. These excitons in the excited state relax to ground state by radiative decay. The wavelength of the emitted radiation depends on the band gap of the employed emissive material (EMs), *i.e.*, energy difference between HOMO and LUMO levels. Like HTMs and ETMs, EMs should be amorphous and possess high thermal stability⁴. 4,4'-bis(2,2'-diphenylvinyl)-1,1'-biphenyl(DPVBi), 9,10-di(naphtha-2-yl)anthracene(ADN), 2-(N,N-diphenyl-amino)-6-[4-(N,N-diphenylamine)styryl]naphthalene(DPASN), are commonly used blue emissive materials¹³ (**Chart 3**).

SHORTCOMINGS OF FLUORESCENT OLEDs

Luminescence is a photo-physical phenomenon, where a molecular system in electronically excited state de-excites to ground state, releasing energy in the form of light. However, in case of electrical excitation, due to statistical distribution of excited spin state population, theoretical achievable limit of emission efficiency for a fluorescent OLED is 25%. However, this limit can be mitigated, when phosphorescent emitters are employed. This is feasible because of possibility of harnessing emission from both singlet and triplet excitons. Phosphorescent emitters due to strong spin-orbit coupling facilitates intersystem crossing (ISC) to excited triplet state, and ultimately allows efficient radiative decay to ground state, (**Figure 4**).

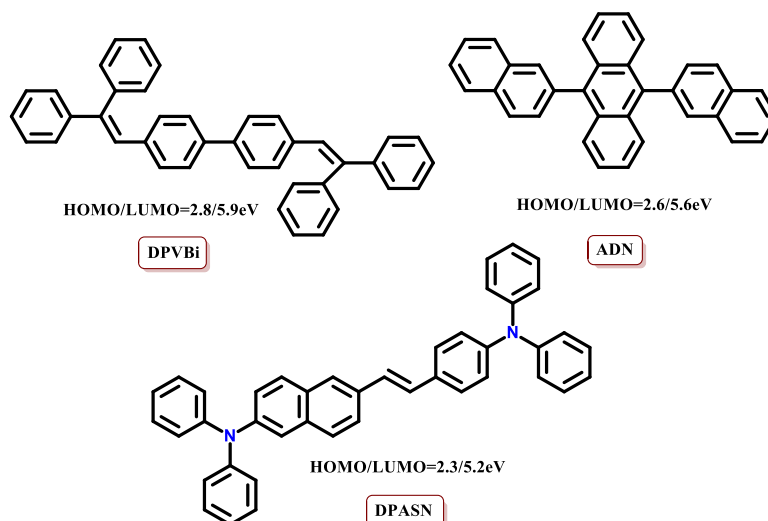


Chart 3: Structures of commonly employed EMs.

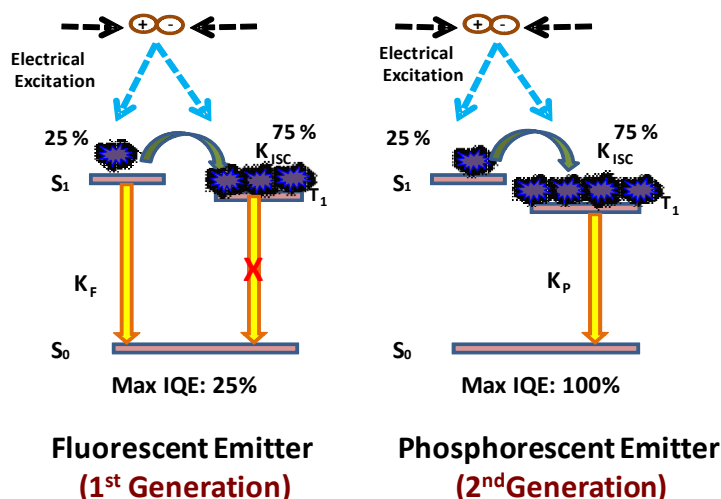


Figure 4. Schematic representation of operation of fluorescent OLEDs vs. phosphorescent OLEDs.

PHOSPHORESCENT ORGANIC LIGHT-EMITTING DIODES (PhOLEDs)

In PhOLEDs, heavy-metal complexes are employed as triplet emitter to facilitate intersystem crossing. However, these triplet emitters are prone to concentration quenching due to triplet-triplet annihilation. Thus to prevent concentration quenching, these complexes are dispersed in a host matrix. Host materials that are employed in a PhOLED device should fulfill certain properties to be useful for the application, which are as following: 1) host material should be amorphous; 2) host material should have higher triplet energy than triplet emitter to prevent back transfer of energy from the triplet emitter to host; 3) host material should be thermally stable and should form morphologically stable uniform pin-hole free films. Materials with high thermal decomposition temperature (T_d) are thermally stable. Similarly, materials with high glass transition temperature (T_g) form morphologically stable films; 4) host materials should have proper HOMO/LUMO energies, which should match with the HOMO/LUMO energies of the adjacent hole-transport or electron-transport layers in the device. This is essential for achieving balanced hole and electron ratio in the devices¹⁴. The structures of commonly employed host materials are shown in **Chart 4**.

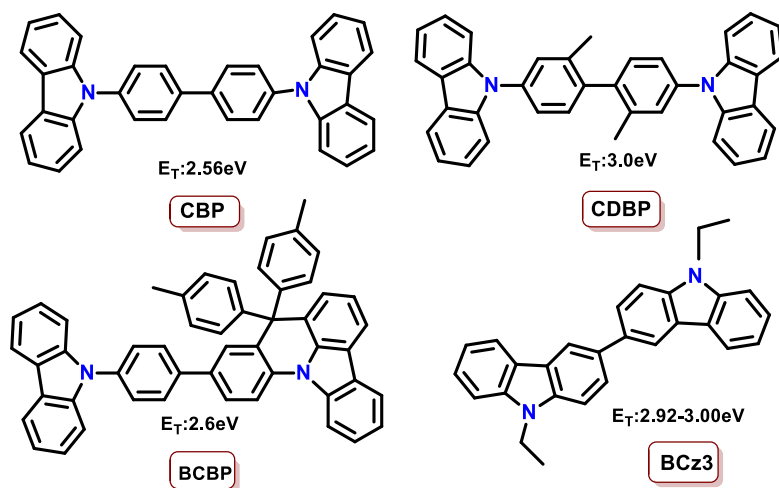


Chart 4: Structures of commonly employed host materials

Triplet emitters that are commonly employed for PhOLED devices are: FIrPic, Ir(ppy)₃ and (piq)₂Ir(acac), cf. chart 5. FIrpic is used in blue electrophosphorescent devices and has triplet energy of 2.65 eV. Ir(ppy)₃ is green emissive triplet emitter and has triplet energy of 2.42 eV, and (piq)₂Ir(acac) is a red emissive triplet emitter and has triplet energy of 2.00 eV¹⁵ (**Chart 5**).

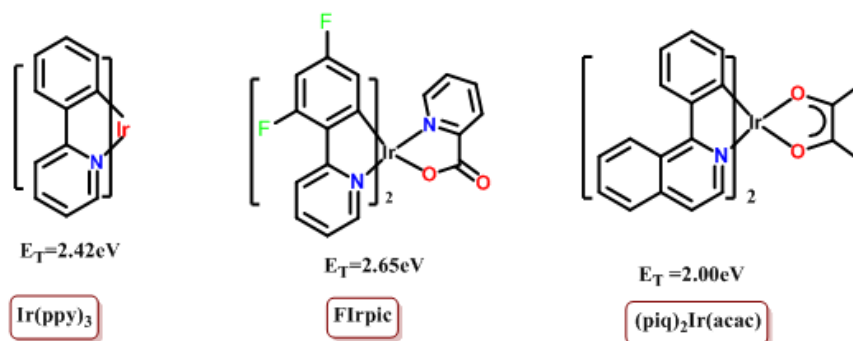


Chart 5: Structures of commonly employed triplet emitters

In General, energy transfer from host to dopant takes place by means of Förster mechanism, Dexter mechanism or by charge trapping. Förster energy transfer is a long range process, whereas dexter energy transfer is a short range electron exchange process (**Figure 5**). In PhOLED devices, Dexter energy transfer dominates over Förster energy transfer¹⁵.

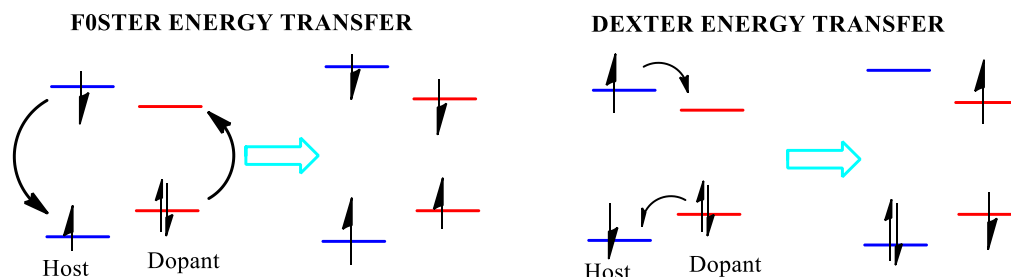


Figure 5: Schematic representation of Foster energy transfer and Dexter energy transfer

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FOOD ADDITIVES: AN OVERVIEW

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INTRODUCTION

According to the Food Protection Committee of the Food and Nutrition Board, food additives may be defined as a substance or mixture of substances, other than a basic foodstuff, which is present in a food as a result of any aspect of production, processing, storage, or packaging. The term does not include chance contaminants.

TYPES OF ADDITIVES

Additives can be divided into nutritional additives, preservatives, coloring agents, flavoring agents and texturizing agents.

1. Nutritional Additives

The term nutritional additives can be used to mean the addition of vitamins, minerals, amino acids, fatty acids, as well as other pure chemical compounds to food in order to improve or maintain the nutritional quality of foods. However, manufacturers soon discovered that along with an improvement in nutritional qualities, nutritional additives often provide functional qualities. The earliest use of nutritional additives was to correct dietary deficiencies. Examples include vitamin D added to milk and vitamin A added to margarine. Nutritional additives can be used to restore nutrients to levels found in the food before storage, packaging, handling, and processing. An early example of this is the enrichment of grain products, corn meal, and rice. Another use of nutritional additives is to improve the nutritional status or correct nutritional inferiority in a food that replaces a more traditional nutritional food, an example would be the fortification of breakfast drink substitutes with folacin and vitamin C. With the advent of nutritional labeling and increased public interest in nutritional properties of food, the food industry rapidly recognized that the addition of nutritional additives can be a selling point. Although it is often thought that the major reason to add nutritional additives to a food supply is to provide nutrients and improve dietary status, nutrients are also added for a variety of other purposes. For example, vitamins C and E may be used for antioxidant properties; beta carotene may be used to provide color.

2. Preservatives

Chemicals such as salt, alcohol and acetic acid have been used for hundred years for preserving meat and vegetables and the pickling of food. These processes rely on reducing the water activity or the pH in the food to inhibit the growth of pathogenic organisms.

3. Colouring agents

Colour additives are dye pigment or substances that impart colour when added or applied to food, drug and cosmetic or to the human body.

Dyes: dissolve in water and are manufactured as powders, granules, liquids or other special purpose form. They can be used in beverages, dry mixes, bakery goods, confectionary, dairy products.

Lakes: are the water soluble form of the dye. Lakes are more stable than dyes and are ideal for colouring products containing fats and oils or items lacking sufficient moisture to dissolve dyes. Typical uses include coated tablets, cake, doughnut mixes, hard candies and chewing gums.

Natural Colourants: Anthocyanins: the anthocyanins comprise a diverse group of glycosidic derivatives of the 2-phenyl benzopyrylium structure. Anthocyanins impart blue, violet and certain red colours to many edible vegetables and fruits.

Table 1. Preservatives in current use

Sl. No.	Name	Properties	Uses	Related Preservative
1	Sorbic acid	Inhibits the growth of yeast and molds	Yoghurt, sweets, pizzas and desserts	Sodium, potassium and calcium salts
2	Benzoic acid	Antibacterial and antifungal action in acid foods.	Jams, jellies, soft drinks	Sodium, potassium and calcium salts
3	Sulphur dioxide	Sterilizing at high levels inhibits fungal growth and no enzymatic browning	Fruits and vegetable products.	Sodium sulphite, sodium metabisulphite
4	Acetic Acid	Antibacterial	Pickles, chutneys, cheese	Salts may be used

Carotenoids: Carotenoids are tetraterpene pigments, which exhibit yellow, orange, red and purple colours. Carotenoids are the most widely distributed pigments in nature and are present in photosynthetic bacteria, some species of archaea and fungi, algae, plants, and animals. Carotenoids are oil soluble colours.

Xanthophylls: They are yellow pigments that occur widely in nature and form one of two major divisions of the carotenoid group, the other division is formed by the carotenes. The molecular structure of xanthophylls is similar to that of carotenes but xanthophylls contain oxygen atom while carotenes are purely hydrocarbons with oxygen. Three kinds of xanthophylls are canthaxanthin, zeaxanthin, lutein. They are also considered as antioxidants. They play significant role in human health, particularly the health of eyes and are linked with reduced risk of age-related macular degeneration and cataracts.

β -carotene: It is the most known carotenoid and the most often naturally occurring carotene. β -carotene is also provitamin A can be metabolized to vitamin A in different tissues (liver). β -carotene is also an antioxidant. β -carotene is predominantly found in orange and yellow fruits and vegetables.

Synthetic Colours: Generally synthetic colours give bright and uniform colours. Food companies prefer to use synthetic food colours because they are cheaper, stable and provide long shelf life compared to natural colours.

4. Flavouring Agents

The flavours of most fruits and vegetables are produced by very complex mixtures of aldehydes and esters of organic alcohols and acids, with a range of

essential oils with complex terpenoid structures. Many of the synthetic compounds used are nature – identical that is they occur naturally in foods or formed in cooking processes.

Flavour Enhancers: It enhances or modifies the original flavor or aroma of a food without contributing flavours of their own. Monosodium glutamate and yeast are examples of flavor enhancers. It is used in masalas, spices, noodles and Chinese cookery.

5. Texturing Agents (Emulsifiers and Stabilizers)

The texture of many processed foods depends on the fact that they are emulsions or foams and if they are to retain these textural properties they must be stabilized in some way. The additives used for this purpose are surfactants, amphipathetic molecules which act at the interfaces of the two phases in the food. The most commonly used emulsifiers are mono and diglycerides and phospholipids such as lecithin.

Stabilizers are usually macromolecules which form a dispersed matrix or gel into which other smaller molecules can be incorporated. Substances used as stabilizers are polysaccharides. Agar and pectin are examples of stabilizers.

Table 2. Permitted and non-permitted food colours

<i>Permitted Food Colours</i>	<i>Non –Permitted Food Colours</i>
Brilliant blue	Rhodamine B
Carmoisine	Amaranth
Fast green	Orange II
Sunset yellow	Metanil yellow

FUNCTIONS OF FOOD ADDITIVES

Additives may be found in varying quantities in foods, perform different functions in foods and ingredients, and function synergistically with other additives. Their functions can usually be classified as one of the following:

- (1) To maintain or improve nutritional quality.
- (2) To maintain or improve product safety or quality.
- (3) To aid in processing or preparation.
- (4) To enhance sensory characteristics.

Additives that affect nutritional quality are primarily vitamins and minerals. In some foods, these may be added to enrich the food or replace nutrients that may have been lost during processing. In other foods, vitamins and minerals may be added for fortification in order to supplement nutrients that may often be lacking in human diets. Preservatives or antimicrobial substances are used to prevent bacterial and fungal growth in foods. These additives can delay spoilage or extend the shelf life of the finished product. Antioxidants are additives that also can extend the shelf life of foods by delaying rancidity or lipid oxidation. Additives that maintain product quality may also ensure food product safety for the consumer. For example, acids that may be added to prevent the growth of microorganisms that cause spoilage may also prevent the growth of microorganisms that can cause foodborne illness. Additives that are used for processing or preparation aids usually affect the texture of ingredients and finished foods. Some of these are classified as emulsifiers, stabilizers, thickeners, leavening agents, humectants, and anticaking agents. Chemicals in this group of

food additives are also used to adjust the homogeneity, stability, and volume of foods. The fourth major function of food additives is to enhance the flavor or color of foods to make them more appealing to the consumer. Natural and artificial coloring substances are added to increase the visual appeal of foods, to distinguish flavors of foods, to increase the intensity of naturally occurring color.

SAFETY OF FOOD ADDITIVES

Food additives have been studied by international experts and organization like Codex and the level for their use in the manufacture, processing, preparation treatment etc laid down. Independent experts who are members of the JECFA (Joint Expert Committee) of FAO and WHO recommend ADIs and standard specifications of food additives. The national food control authorities assess the safety of food additives before permitting their use under the country regulations. While assessing the safety, the regulatory authorities take into account toxicity, acceptable daily intake, international standard and limitations. The Food Safety and Standard of India also lays down specifications for the use of food additives.

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STARCH BASED BIOPLASTICS: AN ALTERNATIVE FOR FUTURE

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Kerala-673635, India**E-mail: dpdas24@gmail.com***INTRODUCTION**

Different types of materials are used for packaging; including metals, glass, wood, paper pulp *etc.* Most of these enter in waste streams after the use. In recent years, the recycling of these type materials has increased, but the recycling rates for most plastic packaging remain low. Plastics are one of the most important petrochemical based products and they are used in in our daily life. Their technical properties like formability, hardness, elasticity, rigidity, heat resistance and chemical resistance, can be varied across a wide range by selecting the correct raw materials, manufacturing process, and additives. They are lighter and more economical than many other materials. For these reasons, they are the material of choice in many industrial and commercial applications. But most of the plastics last for hundreds of years. Most of them are considered to have a detrimental effect on the environment as they do not readily biodegrade.

This presents environmental concerns, resulting in strengthening of regulations on plastic wastes. Biodegradable plastics with functionalities and processabilities comparable to petrochemical based plastic have been developed for various applications. They are either biobased or biodegradable or both. Basically, these are made from renewable raw materials such as starch or cellulose. Interest in biodegradable plastic packaging arises primarily from their use of raw materials and final waste management by composting or anaerobic digestion to reduce land filling.

APPLICATIONS OF BIOPLASTICS

Established packaging applications for bioplastics are shopping bags, which also have a secondary use as a bag to collect compostable kitchen and garden waste. Further applications are thermoformed inserts for chocolate boxes, trays for fruit, vegetables, meat, tubs for dairy produce, sandwich -spread, bottles, nets or pouches for fruit and vegetables.

In the agricultural area, Mulch films, plant pots and seed trays break down in the soil and are no longer seen as waste. Plant trays for flowers and vegetable plants, made from the bioplastics, can be composted in the domestic compost together with kitchen and garden waste.

In the medicinal field, special bioplastics have been used for many years. Such bioplastics can be applied for several tasks; thermoplastic starch (TPS) for instance is a very good alternative to gelatin as a material for pills and capsules. PLA and its copolymers are used as surgical thread, as a carrier for implanted active substances, or to produce resorbable implants such as screws, pins, or plates that are degraded by the metabolism. So, treatments after surgery can be avoided.

In construction and housing area application examples are carpets made from PLA or PTT and other residential and home textiles. Biobased foams such as polyurethane are suitable for the production of furnitures; particle foams made from PLA are used for building insulation.

Bioplastics can be found in paints and varnishes, linseed oil paints, wallpaper paste etc. Sun glasses with high quality optical lenses made from clear bio-polyamide.

BIOPLASTICS FROM STARCH

Bioplastics can be produced from a wide range of plant-based raw materials. On the other hand natural polymers, that is macromolecules that occur naturally in plants etc., are used, and the smaller molecules, such as sugar, disaccharides and fatty acids (plant oils), are used as the basic raw materials in the production of bioplastics. All of these renewable resources can be obtained, modified and processed into biobased plastics. Starch is one of the most common and easily obtained natural polymers, making it attractive as a bio-based alternative to synthetic polymers. Starch, after hydraulic cracking into glucose is also used as a raw material in fermentation processes. And this way new bioplastics such as PLA and PHA are produced. Sugar is also the raw material for the latest generation of bioplastics including the biobased polyolefin PE and PVC, also partially biobased polyester PET, which however not at all biodegradable.

The plasticization of starch is very complex due to the extensive hydrogen bonding between chains. Starch-based bioplastics can be formed by the same processes as current commercial plastics, giving similar mechanical strength to some polyolefin plastics. Starch supply carbonates can also be converted into bioplastics by fermentation and the action of micro-organisms. PLA (polylactic acid) is most important bioplastic on the market. PLA is based on lactic acid, a natural acid, and is mainly produced by fermentation of sugar or starch with the help of micro-organisms.

To keep the future space requirements as low as possible and less environmental hazardness, research and industry are trying to find ways to use mainly agricultural residue and waste materials for the future production of bioplastics. Even though the starch based bioplastics are at a nascent stage in the world, but in the long run this product has a promising future.

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BIOPOLYMERS FOR FOOD PACKAGING

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INTRODUCTION

Biopolymers are polymers that are generated from renewable natural sources, are often biodegradable, and not toxic to produce. They can be produced by biological systems (*i.e.* micro-organisms, plants and animals), or chemically synthesized from biological starting materials (e.g. sugars, starch, natural fats or oils, *etc.*). Biopolymers are an alternative to petroleum-based polymers (traditional plastics). The bio molecules in our body include proteins and peptides, DNA, and RNA.

CLASSIFICATION OF BIOPOLYMERS

Biobased polymers may be divided into three main categories based on their origin and production.

- 1) Polymers directly extracted/removed from biomass. Examples are polysaccharides such as starch and cellulose and proteins like casein and gluten.
- 2) Polymers produced by classical chemical synthesis using renewable biobased monomers. A good example is polylactic acid, a biopolyester polymerized from lactic acid monomers. The monomers themselves may be produced via fermentation of carbohydrate feedstock.
- 3) Polymers produced by microorganisms or genetically modified bacteria. To date, this group of bio based polymers consists mainly of the polyhydroxyalkanoates, but developments with bacterial cellulose are in progress.

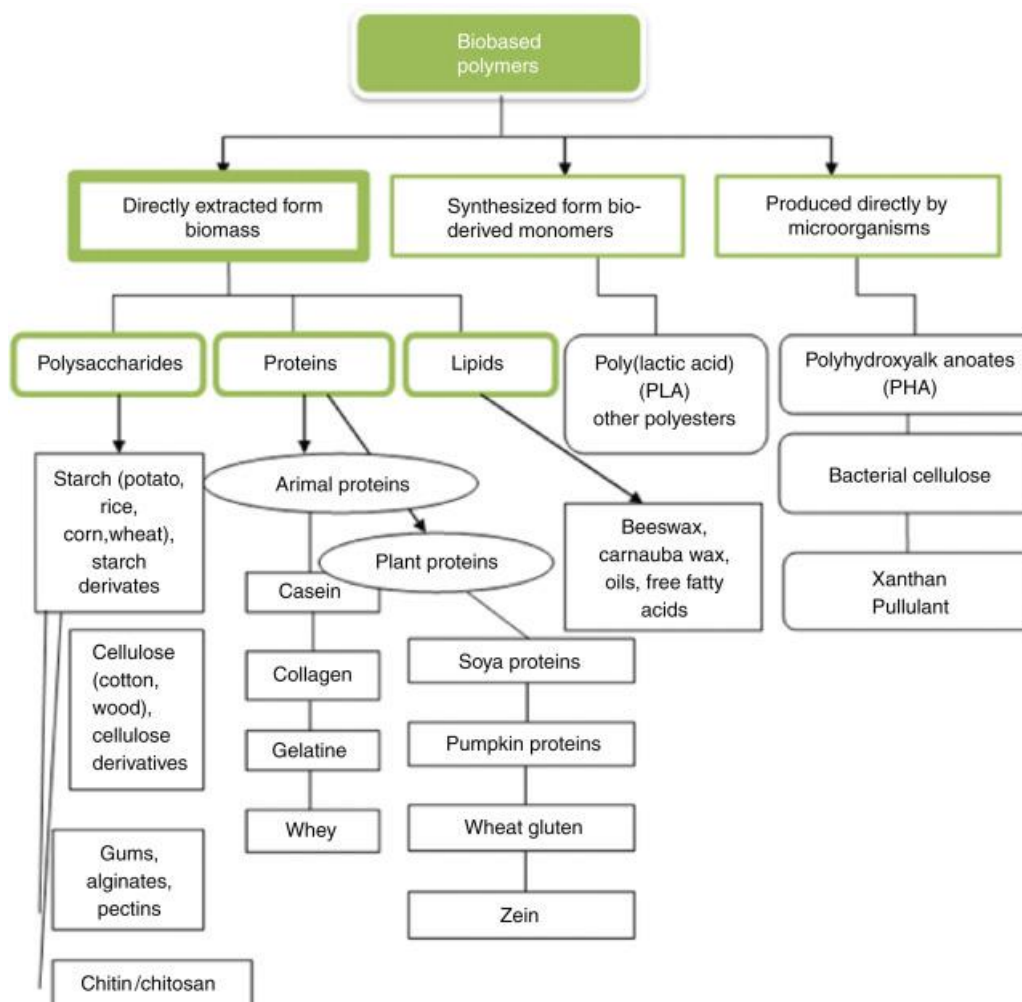
COMMON BIO POLYMERS USED FOR FOOD PACKAGING

1. Polysaccharides

(i) Pectin: Pectin from sugar extraction results a lot of residues, the most relevant is represented by sugar-beet pulp, which is a rich source of pectin. Pectin is an anionic biopolymer soluble in water and it is one of the major structural polysaccharides of higher plant cells and consists on chains of linear regions of (1→4)- α -D-galacturonosyl units and their methyl esters, interrupted in places by (1→2)- α -L-rhamno- pyranosyl units. It is a structural hetero polysaccharide found in the primary cell walls of terrestrial plants such as sugar beet. The biopolymer films of pectin were totally grease proof and also showed improved barrier properties against oxygen and water vapour. The applications of pectin in different industries (food and beverage) were as thickening and gelling agent, and colloidal stabilizer, texturizer, emulsifier.

(ii) Chitosan/Chitin: Chitosan, the β -1-4-linked polymer of 2-amino-2-deoxy- β -d-glucose, is prepared by the N-deacetylation of chitin, the second most abundant natural biopolymer after cellulose. Chitosan is soluble in dilute aqueous acid solutions and has been widely studied

due to its good film forming properties. Chitosan can be used as such in cast free standing films or it can be applied as a coating onto paper/board or plastic films.



(iii) Alginate: Alginate is another polysaccharide, extracted from brown algae such as Laminaria and Macrocystis. Alginate is a binary copolymer and it contains carboxyl groups in each constituent residue. Its structure is composed of β -D-mannuronic acid monomer linked to α -L-guluronic acid monomer, through α 1,4-glycoside linkage. Bacterial alginate was extracted from *Azotobacter vinelandii*. Alginate has been used in the past in food industries as thickening agent, gelling agent and colloidal stabilizer.

(iv) Carrageenan: Carrageenan is derived from red seaweed and has good gas barrier properties. Carrageenans are anionic linear sulphated polysaccharides composed of D-galactopyranose residues bonded by regularly alternating α -(1/3) and β -(1/4) bonds. Carrageenan is one of the three dominant carrageenan species, i.e. κ , ι , and λ carrageenan, which differ in their disaccharide structures. κ -carrageenan is mainly used in food applications. In the food industry, κ -carrageenan is used as a gelling, thickening, stabilising, and water-binding agent in various food products.

(v) Cellulose: Cellulose is one of the most abundant biopolymers in the nature and acts as a reinforcement material in plants and bacteria. Cellulose molecules have amphiphilic character and have a high density of hydroxyl groups, and consist of a chain of β -(1 \rightarrow 4)-linked glucose residues. In recent years cellulose has been extracted from green algae, from the brown alga Laminaria and from others. This type of cellulose has unique and special properties and

hydrophilic nature. Some bacteria belonging to the genera *Gluconacetobacter*, *Sarcina* or *Agrobacterium* are able to produce a particular type of cellulose, designated as bacterial cellulose.

(vi) *Curdlan*: Curdlan is a water-insoluble bacterial glucan polysaccharide produced by *Alcaligenes faecalis* var. *myxogenes* and *Agrobacterium* sp. and is composed of a linear homopolymer of D-glucose with β -1, 3 linkages. Curdlan has heat-gelling and water-binding functionalities very important to the food industry.

(vii) *Gellan*: Gellan is secreted and extracted from the bacterium *Sphingomonas elodea* (previously named *Pseudomonas elodea*). Gellan gum is a linear anionic hetero polysaccharide having a tetrasaccharide repeating unit consisting of rhamnose, D-glucose and D-glucuronic acid in the ratio of 1:2:1. It has the potential for partial or total replacement of existing gelling agents.

(viii) *Pullulan*: Pullulan is a non-ionic polysaccharide produced extracellularly by the fungus *Aureobasidium pullulans*. It consists of a succession of maltotriose type units i.e. α -(1 \rightarrow 6)-linked (1 \rightarrow 4)- α -D- triglucosides. Pullulan is readily soluble in water but insoluble in organic non water-miscible solvents. In present pullulan is used for different applications in medicine, food, cosmetics and ecology, with various purposes, such as: blood plasma substitutes, additives, flocculants, resins, and remediation agents.

(ix) *Starch*: Starch is a well-known hydrocolloid biopolymer and is produced by agricultural plants in the form of granules of various sizes within the endosperm, which are hydrophilic. The most important sources of starch extraction are potatoes, corn, wheat and rice. It is composed of 30% amylose (poly- α -1,4-D-glucopyranoside), a crystalline polymer and 70% amylopectine (poly- α -1,4-D- glucopyranoside and α -1,6-D-glucopyranoside) and less than 1% proteins and lipids, a branched and amorphous polymer. Starch is a great to enforce the textural properties of many foods and is widely used in food and industrial applications as a thickener, colloidal stabilizer, gelling agent, bulking agent and water retention agent.

(x) *Xanthan*: Xanthan gum, is an polysaccharide synthesized by aerobic fermentation of the bacterium *Xanthomonas campestris*. Xanthan consists of 1,4-linked β -D-glucose residues having a trisaccharide side chain attached to O-3 of alternate d-glucosyl residues. The side chains are (3 \rightarrow 1)- α -linked d-mannopyranose, (4 \rightarrow 1)- β -D- mannopyranose and (2 \rightarrow 1)- β -D-glucuronic acid, which account for the anionic properties of xanthan gum. Xanthan gum is largely the most important commercial microbial hydrocolloid used in the food industry as a thickening agent and stabilizer.

2. Proteins

(i) *Collagen*: Collagen is the primary protein component of animal connective tissues. In this tissue there are many types of collagen (over twenty types). Collagen is composed of different polypeptides, which contain mostly glycine, proline, hydroxyproline and lysine. Some differences in amino acid composition are apparent across collagens derived from different sources. There are certain features that are common to and uniquely characteristic of all collagens.

(ii) *Gelatin*: Gelatin is a protein obtained by hydrolyzing the collagen contained in bones and skin. Gelatin obtained from mammalian sources (porcine and bovine), is the most important and most used. This structure is determined by the properties of collagen from which gelatin is obtained. In the last years, in the food industry, the number of new applications for gelatin has increased. The new applications found for gelatin in food products are very diverse, from emulsifiers and foaming agents to stabilizers, and biodegradable films. All this applications

are given by the growing demand to replace synthetic agents with natural and biodegradable ones.

(iii) Soy protein: Soy protein has been used since the 19th in a variety of foods. The main characteristics of soy proteins that are useful in food industry are emulsification and texturizing effect. Soy protein exists as soy flour (SF) which requires less purification, soy protein isolate (SPI) and soy protein concentrate (SPC). Chemically, SPI contains 90% proteins and 4% carbohydrates, SPC contains 70% proteins and 18% carbohydrates, SF contains about 52% proteins and 32% carbohydrates. SF is the least expensive variety of these three forms. Soy protein can be used in the manufacture of adhesives, plastics, and packaging materials and can be a good alternative to the petroleum polymer.

(iv) Whey protein: Whey proteins are a by-product from the cheese industry, and consist of whey protein isolates (WPI) which represent the purer form of such proteins. Another form of whey proteins are whey protein concentrate (WPC). Whey proteins are capable to form elastic films, and they have been employed as raw material for biodegradable packaging because they have good oxygen barrier and moderate moisture permeability.

(v) Zein: Zein is the major storage protein of corn and is a naturally occurring protein polymer obtained as a product of industrial corn processing that has been used to develop various types of thermoplastic products. The high content of non-polar amino acids gives corn zein a relatively hydrophobic nature and this feature lead to obtaining excellent barrier to oxygen but instead lead to poor mechanical properties.

3. Aliphatic Polyesters

(i) Polylactic acid (PLA): Poly (lactic acid) PLA, biodegradable polymers (aliphatic polyester) is obtained from agricultural products such as corn, sugarcane, and others sources. In the process of the fermentation of sugars various monomers are produced, that are converted to polymers. PLA is synthesized from lactic acid produced via starch fermentation from lactic bacteria. Starch is converted into sugar and after that the sugar is fermented to give lactic acid.

PLA can be found as a polymeric helix and can exist in 3 stereochemical forms: poly (L-lactide) (PLLA), poly (D-lactide) (PDLA), and poly (DL-lactide) (PDLLA), with extremely various tensile properties, depending on its degree of crystallinity. PLA is a hard material and its hardness is similar to acrylic plastic, is not soluble in water and it is completely degraded under compost conditions, but there are microorganisms in marine environments can degrade it. PLA polymers are materials that are creating a lot of interest in the packaging industry for its properties and earth-friendly biodegradability. These properties include resistance to oil-based products, seal ability at lower temperatures, and can act as flavor or odor barriers for foodstuffs.

(ii) Polyhydroxybutyrate (PHB): Poly(3-hydroxybutyrate) (PHB) is one of the biodegradable PHA (polyhydroxyalkanoates) and is a naturally occurring β -hydroxyacid (a linear polyester). The general structure of the repeating units of these polyesters is different depending on the type of bacteria and the feed, it is typically $-(CH_2)_n-CH_3$ for most naturally occurring PHAs. There are many microorganisms which accumulate PHB, but the most widely studied bacterium is *Ralstonia eutropha*, due to its ability to accumulate large quantities of PHB. Other microorganisms that accumulate PHB are *Haloferax mediterranei*, *Halomonas boliviensis* and *Bacillus megaterium*.

PHB is a linear, isotactic, semicrystalline biopolymer based on (R)-3-hydroxybutyric acid. With the purpose to improve flexibility, PHB is synthesized with various co-polymers

such as poly-(3-hydroxyvalerate) (HV) in order to decrease of the glass transitions and melting temperature. Current applications of PHB-based polymers or composites include the packaging industry, medicine, pharmacy, agriculture, food industry.

The food industry has seen great advances in the packaging sector since its inception in the 18th century with most active and intelligent innovations occurring during the past century. These advances have led to improved food quality and safety. While some innovations have stemmed from unexpected sources, most have been driven by changing consumer preferences. The new advances have mostly focused on delaying oxidation and controlling moisture migration, microbial growth, respiration rates, and volatile flavors and aromas. This focus parallels that of food packaging distribution, which has driven change in the key areas of sustainable packaging, use of the packaging value chain relationships for competitive advantage, and the evolving role of food service packaging. Biopolymers have highly influenced the packaging sector greatly. Environmental responsibility is constantly increasing in importance to both consumers and industry.

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ESTIMATION OF CALCIUM IN SOME MILK SAMPLES

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INTRODUCTION

Calcium, the most abundant mineral in our body, makes up about 1.5 to 2% of the body weight and 39% of total body minerals. Approximately 99% of the calcium exists in the bones and teeth. The remaining 1% of calcium is in the blood, extracellular fluids and within the cells of all tissues, where it regulates many important metabolic functions¹.

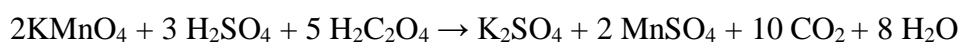
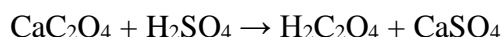
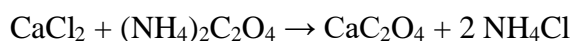
Even though only 1% of calcium in the body is found outside the bone, this form of calcium is critical for many functions in the body. Therefore, its level is maintained in a narrow range in the blood and tissues.

Calcium deficiency disease, also known as hypocalcemia, occurs when we don't intake enough calcium. This increases the risk of developing diseases such as osteoporosis. We should consume the recommended amount of calcium per day through the food we eat. If necessary, we can take calcium supplements to get enough calcium².

The natural aging process can cause calcium deficiency disease. Most of the calcium in our body is stored in our bones. As we age out, bones become thin or less dense. So we should increase our daily calcium supplement. It is vital for women to consume the recommended daily amount of calcium during middle age. This is when most women approach menopause. A decline in the hormone estrogen during menopause causes women's bones to thin faster. Most menopausal women should increase the amount of calcium in the foods they eat to reduce the risk of brittle bone disease (osteoporosis) and calcium deficiency disease³.

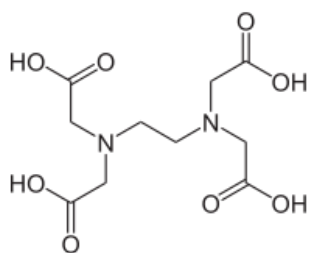
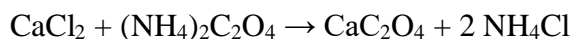
ESTIMATION OF CALCIUM

Calcium can be estimated by volumetric and gravimetric methods. Volumetric estimation can be done by permanganometry or complexometry. In permanganometry, calcium is precipitated in basic medium as calcium oxalate, dissolved in hot H₂SO₄ and the oxalic acid formed is titrated against standard KMnO₄ solution⁴.

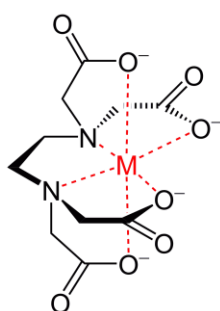


In complexometry, calcium is estimated by titrating against standard EDTA solution using murexide (ammonium purpurate) as the indicator. The metal-indicator complex, being less stable, is converted to more stable metal-EDTA complex during titration.

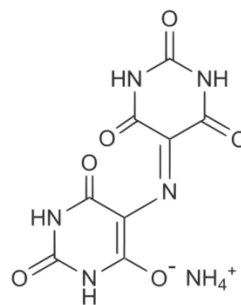
In gravimetry, the precipitated calcium oxalate is ignited in a previously weighed silica crucible and is estimated⁴ as CaCO₃.



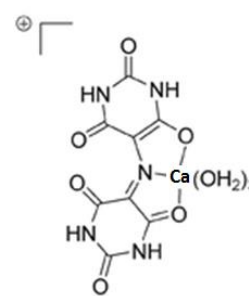
Structure of EDTA



Structure of Metal-EDTA complex



Structure of Murexide



Structure of Metal-indicator complex

DETERMINATION OF CALCIUM CONTENT IN MILK

Weigh accurately a definite amount of milk samples using an electronic balance. Transfer it into a 100 mL beaker and dissolved in minimum amount of conc. HCl. The solution is strongly heated to convert the calcium into soluble CaCl_2 . It is then quantitatively transferred into a 100 mL standard flask and make up to the mark. Shake the solution for uniform concentration. Pipette out a definite volume (depending on the amount of calcium content) into a 250 ml conical flask, add NaOH pellets until the solution become alkaline (confirmed by using a pH paper), add about 50 mg of murexide indicator and titrated against the standard EDTA solution from the burette till the colour changes from red to purple. Titrations are repeated till concordant values are obtained. From the titre values, amount of calcium in the various milk samples can be calculated⁴⁻⁶ (Table 1).

MILK SAMPLES

Buffalo Milk



Cow Milk



Goat Milk



Milma Milk



Good Life Milk



PDDP Milk



Table 1: Calcium content in different milk samples

Sl. No.	Name of milk	Weight of the milk (g)	% of calcium	
			Experimental	Theoretical
1	Cow milk	20.1630	0.1140	0.120
2	Goat milk	20.3216	0.0788	0.134
3	Buffalo milk	20.4887	0.1730	0.180
4	PDDP milk	20.4412	0.0790	0.104
5	Good life milk	20.4743	0.0995	0.126
6	Milma milk	20.3066	0.1272	0.150

Milk is one among the calcium rich food item. We examined the milk of different animals (cow, buffalo and goat), as well as the milk samples of different companies. Out of three milk samples of different animals studied, buffalo milk contains high calcium content

and goat milk contains the least. Discrepancy between theoretical and experimental value is less in cow milk and more in goat milk. Out of the three different brands of milk samples studied, Milma milk is with most calcium content and PDDP milk with the least. Discrepancy between theoretical and experimental value is less in milma milk and more in good life milk (Figure 1).

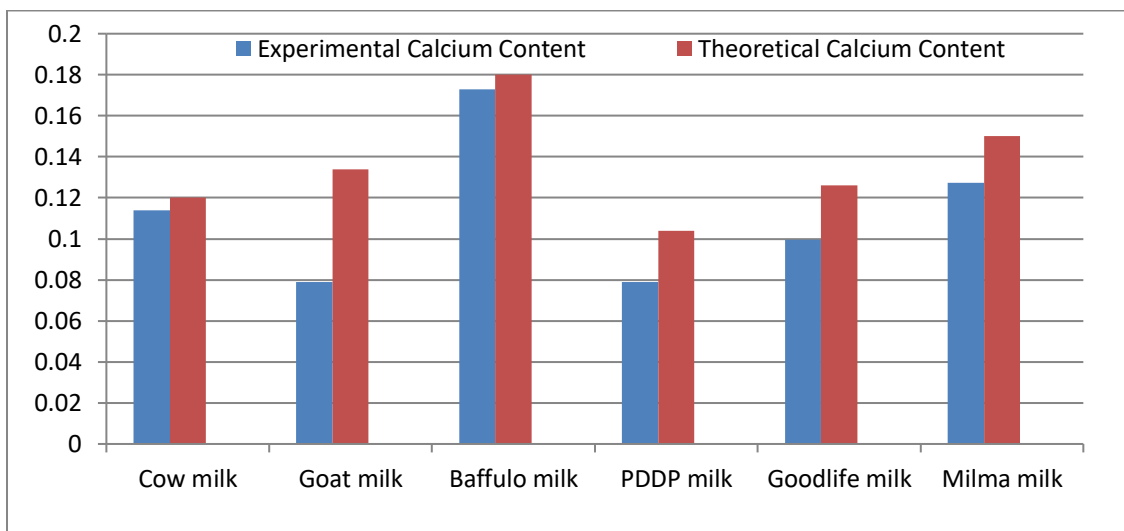


Figure 1: Comparison between theoretical and experimental calcium content in milk samples

The amount of calcium that is completely assimilable by human body is a big concern yet to be studied.

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CHITIN AND CHITOSAN: KEYS FOR GREENER WORLD

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Plastics are not always produced from fossil materials such as petroleum. Quite the contrary, the first plastics were biobased. Celluloid is regarded as the world's first "plastic", discovered by Alexander Parkes in 1855. These biobased plastics were forgotten in the age of the petroleum boom. Only from 1980, bioplastics become once again a focus of research and development. The primary interest at that time was biodegradability and compostability.

The production of biodegradable polymers and photodegradable polymers which are decomposed by microorganisms and sunlight is a priority among researches. Chitin and Chitosan are such a type of polymers which is biodegradable in natural environment. Chitin is widespread polysaccharide and produced as much as cellulose in nature. It is the main component of the exoskeleton of animals like insects and crustaceans (shrimp, crab, and lobster etc). More than 10^{11} tons per year of chitin is produced annually in aquatic region. The use of this waste for renewable products is a dual-purpose opportunity. Therefore, crab, shrimp, and fish scale wastes are ideal raw material for extraction of chitin. Extracted chitin can be used to produce chitin-derived products, such as chitosan.

Chitin is one of the most abundant natural occurring polysaccharide that contains amino sugars. It is found in association with proteins and minerals such as calcium carbonate in crustaceans. Chitin is composed of N-acetylglucosamine [$\beta(1\rightarrow4)$ -linked 2-acetamido-2-deoxy- β -D-glucose].

Chitosan, a linear bio-polyaminosaccharide is derived by alkaline deacetylation of chitin. Chitosan is cheap, biodegradable and nontoxic to environment. Chitosan is a weak base and insoluble in water and organic solvent. But it is soluble in dilute aqueous acid medium due to the protonation of its amino groups. Chitosan is a linear polymer of $\alpha(1\rightarrow4)$ -linked 2-amino-2-deoxy- β -D-glucopyranose and is easily derived by N-deacetylation. It consists of glucosamine and N-acetylglucosamine.

Most of the naturally occurring polysaccharide e.g., cellulose, agarose, dextrin, agar, and pectin are acidic in nature, whereas chitin and chitosan are examples of highly basic polysaccharides. They contain more than 5000 glucosamine unit. The reactions of chitosan are more versatile than cellulose due to the presence of NH_2 groups. Many efforts have been made to prepare functional derivatives of chitosan by chemical modifications, graft reactions, ionic interactions, and only few of them are found dissolve in conventional organic solvents. These derivatives have a wide range of uses. It has ability to carry a large number of amine groups on its chain, and can form multiple complexes. At acidic pH, the protonated form, it can combine with polyanion to form complexes. At higher pH level it can make complexes with heavy metals. The pair of free electrons present in the amino group is assumed to be the origin of the bonds. Therefore, it is a good biosorbent of metal ions. Chitosan may be readily derivatized by utilizing the reactivity of the primary amino group and the primary and

secondary hydroxyl groups present. Chitosan is a pseudo plastic material and is an very good viscosity enhancing agent in acid environments. The viscosity of chitosan solution can affect by the molecular weight, degree of deacetylation, pH, ionic strength, concentration and the temperature. Generally, there is a decrease in the viscosity of the solution by the increase in temperature and increase with an increase in chitosan concentration. As the chitosan is hydrophilic in nature, therefore it has the ability to forms gels at acidic pH.

The interest on chitin originated from the study of the behaviour and chemical characteristics of lysozyme present in the human body. It dissolves certain bacteria by cleaving the chitinous material of the cell walls. A variety of medical applications for chitin and chitin derivatives have been reported over the last few decades. Recent applications of chitosan are in ophthalmic, nasal, buccal, mucosal-vaccine and gene carrier. Chitosan can be used to inhibit fibroplasias in wound healing and to promote tissue growth. The poor solubility of chitin is the major limiting factor in its utilization and investigation of its properties and structure. But various applications of chitin and modified chitins have been reported, e.g., as raw material for man-made fibres. Fibres made of chitin and chitosan are useful as absorbable sutures and wound-dressing materials. These chitin sutures can control attack in bile, urine and pancreatic juice, which are difficult with other absorbable sutures. Chitin and chitosan fibres have potential applications in waste water treatment by the removal of heavy metal ions through chelation process. Their use in the apparel industry, with a very large scope, could be a long run possibility.

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FATE OF MICROPLASTICS IN SOIL

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INTRODUCTION

Microplastics (MP) are emerging pollutants, and since they pose a great danger to whole habitats, their existence in water and soil ecosystems has recently attracted significant attention. Recent research has focused on the identification, occurrence, characterization and toxicology of microplastics in marine and freshwater environments, but our understanding of the ecological impact of microplastics in soil ecosystems is still limited compared with that in aquatic ecosystems. In order to resolve the possible ecological and human health risks posed by microplastics in soil, we have compiled literature, analysis of sources, migration of microplastics in soil, negative impacts on soil health and function, trophic transition in food chains and the related adverse effects on soil species. This Chapter aims to address gaps in knowledge, shed light on the fate of microplastics in soil, and propose future studies on microplastic pollution. Furthermore, this chapter is focused on what happens to microplastic when once it entered into soil environment.

TROPHIC LEVEL TRANSFER OF MP

Microplastic particles will be transferred to higher organisms through the food chain. *Lwanga et al.* performed one study on the trophic transfer of MPs in the terrestrial food chain, in which the concentrations of MPs in gardening soil, earthworm casts, and chicken (*Gallus gallusdomesticus*) faeces were analyzed. The concentrations increased along the trophic levels, and the highest concentration of MP was confirmed in chicken faeces. In particular, chicken gizzards also contained MPs, and this indicated that the evidence of transfer of MPs to humans is through food because gizzards are used for human consumption.

TRANSLOCATION AND ACCUMULATION OF MPs IN ORGANISMS

Maab et al. used two collembolan species, *Folsomia candida* and *Proisotomaminuta*, and observed the transport of urea-formaldehyde particles. The transport of particles was strongly dependent on the type of particle, size of particles, and size of organisms. Nevertheless, the authors confirmed the horizontal transport of plastic particles by soil microarthropods. *Rillig et al.* also studied the transport of PE-MP by soil organisms *L. terrestris*, which were cultured in 2.5 kg of soils covered with 750 mg of various sizes of PE-MPs particles. After 21 days of exposure, MPs were detected in the middle and bottom layers of soils, and the smallest particles (710–850 μm) reached the deepest layers of the soil. The mechanisms of plastic transport in soil were not demonstrated, but they suggested that MPs might be transported through the activities of earthworms such as ingestion/egestion, burrowing, adherence, and casts making. So far, despite their ecological importance, the exposure of soil filter feeders such as nematodes, rotifers, and ciliates to MPs and nanoplastics has not yet been determined. Filter feeders in marine ecosystems have been shown to ingest microparticles, while filter feeders in freshwater ecosystems, *Daphnia*

magma and *Thamnocephalus platyurus* has been shown to be sensitive to nanoplastics. Organisms with other feeding modes are also susceptible to microplastic ingestion. Taylor *et al.* found synthetic microfibers on and inside six out of nine deep-sea organisms that belong to the phyla Cnidaria, Echinodermata and Arthropoda with predatory and feeding mechanisms. As such, woodlice, snails, caecilians, and other soil organisms with similar feeding mechanisms would be subjects of interest in agroecosystems. Information about the bioavailability and bioaccumulation of MPs in soil organisms is generally lacking. We know that nanoplastics can enter cells, as fluorescent nanoplastic polymers have been used as molecular probes for a wide range of biological studies with mammalian cells, for example, to measure blood flow in tissue and as tracers for phagocytic processes. The translocation of a range of microparticles by mammalian gut into the lymphatic system has been demonstrated in rabbits, dogs, and rodents. There is no experimental evidence of nanoplastics being transferred from invertebrates to vertebrates. However, there is evidence of the transfer of MPs from contaminated land to vertebrates and potentially from earthworm to chicken.

DISTRIBUTION OF TOXIC CHEMICALS BETWEEN MPs AND SOIL

Many types of toxic chemicals, such as polychlorinated biphenyls, polycyclic aromatic hydrocarbons, dichlorodiphenyltrichloroethane, perfluoroalkyl substances, pharmaceuticals and personal care products, and heavy metals, can be absorbed by microplastics and also may serve as a sink for certain toxic chemicals in sea water¹. The concentration of PCBs and dichloro diphenyl dichloroethylene collected in PP pellets can be up to 105-106 times greater than concentrations in ambient seawater because of the hydrophobic nature of plastic surfaces². Unlike water, however, SOM will dominate the sorption of hydrophobic organic compounds (HOCs) when the content of organic carbon is greater than 0.1 percent³. Microplastics are likely to compete with SOM for the absorption of chemicals, especially HOCs, once they reach the soil environment⁴. Many kinds of organic compounds have been reported to be sorbed by microplastics, showing a distinct sorption affinity pattern^{5&6}. The partition coefficients (Log K_{MP}) of HOCs (e.g., polycyclic aromatic hydrocarbons and hexachlorocyclohexanes) on PE, PP, and PS microplastics showed strong linear correlations with their Log K_{ow} values, with R² values of 0.92, 0.94, and 0.84 respectively, as reported by Lee *et al.* (2014)⁷.

STORAGE OF MPs IN SOILS

Incorporation of plastics into soil aggregates may promote long term storage. Aggregation may limit exposure to soil fauna and hinder the transport of plastic particles. Nanoparticles aggregate rapidly in aquatic environments and heteroaggregation has been noted as an important control on nanoplastic fate. Aggregate stability is associated with soil system health, so the role of aggregates as micro (nano) plastic stores is likely to be dynamic and environment-dependent. Accumulation may also occur through burial where successive flood events bury contaminated layers in alluvial soils. A theoretical assessment of microplastic transport and erosion, based on the frame of a hydrological/sediment transport catchment model, suggested the potential for soils to effectively retain, and therefore store, micro(-nano)plastics. However, experimental data to confirm these findings are not yet available. Microplastics are preserved in marine and lacustrine sediment profiles. Particle burial limits degradative forces and thus increases preservation potential. It is probable that a similar effect will occur in soil systems, establishing soils as a sink for contamination. The role of soil characteristics, such as pH, and soil microbial communities in maintaining degradation must be assessed. Furthermore, disturbance of buried layers may remobilize stored micro(nano)plastics. For example, alluvial soils may be reworked and agricultural practices such as tilling can bring buried particles back to the surface. The accumulation of

plastics in soils must also be examined in the context of ecological risk through long term exposure. While the discussion of the state of ecotoxicological research for microplastics in soils is not the primary focus of this paper, the increasing number of publications in this area demonstrates international interest.

TRANSLOCATION AND EROSION

Erosion by water and wind will transport particles across soil systems and eventually towards streams and rivers. The dynamics of these processes have not yet been investigated; however, inferences can be drawn from the wider domain of microplastics research. Recent work examining the sinking velocities of microplastics in the marine realm has established particle shape as a dominant control. It is likely that shape is also relevant for the erosion of micro(nano)plastics by water in soils. While the effect of erosion and entrainment of microplastics mediated by size and density has been assessed through a theoretical model, the influence of shape on translocation over soils or sediments as well as on their hetero-aggregation has not yet investigated. However, these processes will lead to a winnowing effect based on particle morphology and properties, such as that seen for natural soil particles. The irregular shape and low mass of particles such as fibres lead to a preferential entrainment by wind erosion. Hence, the scale of wind and water erosion is significant in determining enrichment or depletion of specific particle types. Furthermore, micro(nano)plastics do not necessarily represent inert polymers upon entry to soil systems. Particles that have been through wastewater treatment or have been exposed to the environment may have become significantly biofouled or gained a surface charge. This can alter the nature of particle mobilisation and erosion. Soil fauna also contribute to the transport of microplastics within soil systems. Plastic particles may adhere to an organism's exterior or be transported internally through intake and subsequent egestion. These mechanisms have been shown to contribute towards the dispersal of plastic particles from a point source. Bioturbation also results in vertical transport. This occurs through the process of burrowing, which establishes biopores in the soil matrix and incorporates microplastics into burrow walls and casts. This process significantly increases the downward translocation of plastic. Micro(nano)plastic ingestion may represent a removal from soils when this results in systemic translocation or trophic transfer. The uptake of microplastics by plants is unlikely but may occur for nano-sized particles. However, data are insufficient to establish the significance of this process for the overall budget of particles in a soil. Degradation Environmental degradation has been discussed for aquatic and sedimentary environments and many of these processes also occur in soils. The topsoil likely represents a key degradative environment, due to the direct exposure to UV radiation, increased oxygen availability, and higher temperatures. Soil microbial communities and terrestrial organisms may accelerate biodegradation of brittle plastics. Furthermore, agricultural processes such as tilling may fragment plastic debris. All these processes contribute to the progressive fragmentation of plastic from macro-to nanoscale.

LEACHING TO GROUND WATER

Leaching is an important process driving contaminants with certain properties to groundwater. Micro (nano) plastics have not yet been analysed in groundwater samples but transport through biopores has been identified as a possible mechanism for groundwater contamination. Theoretically, assuming plastics as mainly inert materials, the potential for leaching will be modulated by soil texture properties and particle size, density, and shape. Additional soil properties such as zeta potential and ionic strength may, in principle, influence transport of non-inert particles. Fundamental speculative reasoning suggests that nanoscale inert plastics with a density higher than water may be effectively leached to

groundwater. This can represent a potential pathway to human exposure. Future research This paper summarises existing studies on soil microplastics and outlines the potential mechanisms for soil micro(nano)plastic dynamics. Further work is crucial to elucidate sources, behaviour, and fate. The following steps in soil micro (nano) plastics research should be prioritized: - Filling the methodological/technological gaps hindering an accurate assessment of micro(nano)plastics in soil samples, including methods for car tire debris and nano-scale materials. - Delivering baseline studies on soil exposure along a gradient of land uses and soil management. This will establish the scale of contamination and can point towards potential source apportionment: for example, fibres and microbeads as indicators of sludge application or tire dust as an indicator for road runoff. - Unravelling the processes controlling budgets of microplastics in soil environments, including the assessment of microplastic transfer from soil to humans through the uptake in foodwebs and through leaching to the groundwater. - Developing a solid experimental and conceptual framework to characterize risk and impacts from soil micro (nano) plastics for humans and the environment. Timely translating of findings to stakeholders (i.e. industry, wastewater utilities, and farmers) and governance endorsing knowledge-based decision making.⁸

MP concentration differed at different soil depths, indicating that the MPs moved downward through unknown mechanisms. The migration behaviour of MPs in soil is complex, and their vertical and horizontal distributions may be affected by many factors. Bioturbation enables the migration of MPs in soil, namely, MPs are transferred and transported by soil fauna (e.g., larvae, earthworms, vertebrates) and poultry, either by attachment to the outside of animals or by ingestion and excretion. Mites (i.e., *Hypoaspis aculeifer*) and collembola (i.e., *Folsomia candida* and *Proisotomaminuta*) were recently reported to promote the migration and distribution of MPs in soil by scraping or chewing on them. Digging mammals (e.g., ground squirrels and moles) exhibit similar behaviour. Behaviour associated with earthworms, including external attachment, ingestion and excretion, promotes the lateral and vertical distribution of MPs in the soil. In addition, larval feeding behaviour was reported to cause MPs carried by adult mosquitoes to spread out into the environment. Earthworm waste (vermicast) contains concentrated MPs that can be eaten by soil microarthropods. Therefore, we speculate that when there exists a predator-prey relationship among soil microarthropods, the complex food web in the soil ecosystem composed of diverse species relationships will definitely promote the migration of MPs. Similarly, the transport of MPs is affected by root disturbances (such as root movement, expansion, and absorption) and rhizosphere hyphae. However, this is only a corollary, and future perspectives should reveal the influential mechanism of plant roots on MP migration. Tillage activities, such as tilling and ridging, make it easy for MPs to be carried into deep soil. In addition, the harvest of tubers (e.g., potatoes and yams) may facilitate the vertical migration of MPs. A recent study demonstrated that the wetting-drying cycle can accelerate the downward migration of MPs. Apparently, these driving factors facilitate the movement of microplastic granules. Nevertheless, the extrinsic forces have little effect on the downward motion of MPs. For example, traditional farming practices affect only the topsoil. Defined as the loss of mineral and organic solutes due to percolation in soil, leaching has a strong role in facilitating the vertical movement of MPs. Soil is a porous medium with μm -sized pores, thus allowing the transport of soluble materials and granules. Therefore, soil texture determines the pore size, which directly affects the migration of MPs. The retention of MPs in quartz sand media can be significantly improved by increasing the ionic strength. This may be due to the high strength of ions pressing against dual thickness, resulting in decreasing energy barriers and deepening depths in elementary and subprime polar regions. The ion strength of soil pore water may be similarly affected, although there is no experimental evidence to

prove this. In addition, several studies show that surface roughness, biofiltration, organics, saturation and hydrodynamic conditions of the medium affect the migration and fixation of MPs in quartz sand. Studies of colloidal migration in quartz sand indicate that strain and physico-chemical sedimentation control the critical interactions of colloidal migration and fixation. The results revealed that membrane strain, solid-liquid interface adhesion, air-water interface capture and pore repulsion are the main mechanisms. Keller et al. (2020) synthesized a mixture of passive inorganic tracer and MP fiber, and used inductively coupled plasma mass spectrometry (ICP-MS) to rapidly and quantitatively analyzed the MP transport behavior in simulated soil columns (glass beads). The mobility and transport of MPs into the soil may depend on their size and aggregation state (e.g., organic solids). Transport may also be related to shape or polymers, and to this end, heterogeneous aggregates and/or adhesion to organic matter should be further investigated. Another factor is the presence of highly variable conditions in the soil, such as soil type, temperature, and water status which affect the fate and behavior of MP particles. The above research provides information to explore the migration mechanism of MPs in soil. However, soil as a heterogeneous medium is far more complex than quartz sand. Recently, two simulation studies showed that soil organic carbon (SOC), clay, Fe_2O_3 , pH, and CEC play important roles in the adsorption and migration of polystyrene MPs (PSMPs). More research is recommended to reveal the contribution of inherent properties (such as external texture and granule size) and external factors (such as porosity, saturation and ion strength) to the migration of MPs in soils. Soil MPs may migrate through dynamic driving forces such as dustfall, wind and water or soil erosion. MPs, especially microfibers, on the surface of the soil can be suspended in the atmosphere by upper air wind for a period of time before deposition through rain or dust. MPs also enter coastal waters through surface runoff. These migration risks are believed to be relatively high, especially in cultivated soils with extensive irrigation canals, ditches and overland runoff. At present, there is low pollution (12 items/L) in groundwaters, but this does suggest the transfer of MPs. The properties of MPs themselves are also important factors affecting their migration in soils.

CONCLUSIONS AND PERSPECTIVES FOR FUTURE RESEARCH

The current ecological risks from plastic pollution are expected to continue into the future due to expected increases in plastic production, significant durability of plastic particles, degradation of existing plastic pollution and increase in MPs and NPs worldwide. The research of MPs in the environment is still in its infancy. At present, plastic debris are relatively well defined as a group of mixed substances composed of synthetic or heavily modified natural polymers, and they are solid and insoluble at 20°C. Persistent water-soluble polymers like polyacrylamides (PAM) and polycarboxylates would not be considered microplastics and therefore will not gain as much attention as they should. Because of annual production volumes well into the millions of tonnes, especially considering that PAM releases its monomer acrylamide (a powerful neurotoxin) under anaerobic conditions, its harmful environmental effects should not be overlooked. Obviously, we know that microplastics come from a multitude of sources, including products used for a variety of applications (e.g., tires, textiles, packaging), comprise different sizes, shapes, colours, and types of material (molecular composition and structure), and include mixtures of diverse chemicals. They migrate through nature via diverse pathways and affect biota and ecosystems in different ways. Like pesticides with diverse molecules, structures and applications, microplastics should be reconsidered as a diverse suite of contaminants rather than a contaminant. Current research on plastic pollution is limited by the conceptual plastic fate and transport models from land to ocean. Thus far, this holistic and integrated approach has not been widely used and adapted, although some models to follow their fate and transport

through the various ecosystem processes it undergoes, as well as potential exposures to human. The introduction of this concept may have important implications for policy and management of this issue. It is therefore suggested to consider the plastic pollution problem as a concept of an environmental or biogeochemical cycle, that is, identify the continuous and complex movement of plastic materials (a diverse contaminant suite of large, medium, micro- and nanoplastic) between different abiotic and biotic ecosystem compartments (including humans), based on atmospheric sciences and biogeochemistry, trophic transfer, and human health and exposure. Moreover, this cycling approach will also aid in identifying and understanding the relationships between plastic manufacturing and pollution to other serious environmental problems such as climate change, species loss, coral disease, pathogens and parasites, and antibiotic resistance.⁹

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NUTRIENT DRUG INTERACTION

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A drug interaction is a situation in which a substance affects the activity of a drug, i.e. the effects are increased or decreased, or they produce a new effect that neither produces on its own. Regarding food-drug interactions physicians and pharmacists recognize that some foods and drugs, when taken simultaneously, can alter the body's ability to utilize a particular food or drug, or cause serious side effects.

Major side-effects of some diet (food) on drugs include alteration in absorption by fatty, high protein and fiber diets. The most important interactions are those associated with a high risk of treatment failure arising from a significantly reduced bioavailability in the fed state. Such interactions are frequently caused by chelation with components in food. In addition, the physiological response to food intake, in particular, gastric acid secretion, may reduce or increase the bioavailability of certain drugs. The gastrointestinal absorption of drugs may be affected by the concurrent use of other agents that, have a large surface area upon which the drug can be absorbed, bind or chelate, alter gastric pH, alter gastrointestinal motility, or affect transport proteins such as P-glycoprotein.

Several fruits and berries have recently been shown to contain agents that affect drug-metabolizing enzymes. Grapefruit is the most well-known example, but also sevillean orange, pomelo and star fruit contain agents that inhibit cytochrome P450 3A4 (CYP3A4), which is the most important enzyme in drug metabolism. The novel finding that grapefruit juice can markedly augment oral drug bioavailability was based on an unexpected observation from an interaction study between the dihydropyridine calcium channel antagonist, felodipine, and ethanol in which grapefruit juice was used to mask the taste of the ethanol. Subsequent investigations showed that grapefruit juice acted by reducing presystemic felodipine metabolism through selective post-translational down regulation of cytochrome P450 3A4 (CYP3A4) expression in the intestinal wall.

Among all fruit juices, grape fruit juice possesses high interaction with almost all types of drugs. Taniguchi in 2007 reported a case of purpura associated with concomitant ingestion of cilostazol, aspirin and grapefruit juice in 79 years old man. His purpura disappeared upon cessation of grapefruit juice, although his medication was not altered. The most probable cause of his purpura is an increase in the blood level of cilostazol because of the inhibition of cilostazol metabolism by components of grapefruit juice. Furanocoumarins present in Grape Fruit Juice inhibit the intestinal CYP 3A4 and have been shown to increase the oral bioavailability of medications that are CYP 3A4 substrates like Felodipine, midazolam, cyclosporine and raise their concentrations above toxic levels. Grape Fruit juice is generally contraindicated to patients taking psychotropics and it is advised to inform patients about described interaction. The in vitro data suggest that compounds present in grapefruit juice are able to inhibit the P-gp activity modifying the disposition of drugs that are

P-gp substrates such as talinolol. Users are advised to avoid drinking grape fruit juice within 1-2 hr(s) of taking these anticonvulsants.

Furanocoumarines and active bioflavonoids present in Grape Fruit Juice are also inhibitors of OATP and when ingested concomitantly, can reduce the oral bioavailability of the OATP substrate, fexofenadine. Overall, a series of flavonoids present in Grape Fruit Juice are identified as esterase inhibitors, of which kaempferol and naringenin are shown to mediate pharmacokinetic drug interaction with most of the calcium channel antagonist and the statin groups of drugs such as enalapril and lovastatin due to their capability of esterase inhibition.

Cholesterol-lowering agent lovastatin should be taken with food to enhance gastrointestinal absorption and bioavailability. The absorption of rosuvastatin, another anti-hyper lipidemic agent, was significantly decreased in the fed state compared with the fasting state, which suggests that rosuvastatin should be administered on an empty stomach. Warfarin is commonly used to treat or prevent thromboembolic events. There is a possible interaction between warfarin and a high-protein diet. The potential for increased dietary protein intake to raise serum albumin levels and/or cytochrome P450 activity has been postulated as mechanisms for the resulting decrease in international normalized ratio (INRs).

Eating charbroiled food may decrease warfarin activity, while eating cooked onions may increase warfarin activity. Soy foods have been reported both to increase and to decrease warfarin activity. The significance of these last three interactions remains unclear. The combination of warfarin administration and cranberry juice ingestion appeared to be associated with an elevated INR without bleeding in elderly patient.

Antidepressant activity of monoamine oxidase inhibitors (MAOIs) was initially noted in the 1950s. Although older monoamine oxidase inhibitors (MAOIs) are effective in the treatment of depressive disorders, they are under-utilized in clinical practice due to main concerns about interaction with tyramine-containing food (matured cheese, red wine, rippled bananas, yogurt, shrimp paste and salami) or so called cheese reaction, since they are capable of producing hypertensive crisis in patients taking MAOIs.

Patients placed on anti hypertensive drugs will benefit from concomitant moderate sodium restricted diets. Propranolol serum levels may be increased if taken with rich protein food. A change in diet from high carbohydrates/low protein to low carbohydrate/high protein may result in increased oral clearance. Smoking may decrease its plasma levels of by increasing its metabolism. The intestinal absorption of celiprolol (beta-blocker) is inhibited when it is taken with orange juice. Hesperidin, present in orange juice, is responsible for the decreased absorption of celiprolol. The absorption of ACEs inhibitors is increased when taken on an empty stomach. While GFJ increases the bioavailability of felodipine (Ca2 channel blocker).

Licorice extract, a common ingredient of dietary supplement contains glycyrrhizin and glycyrrhetic acid. It is a potent inhibitor of 11- β -hydroxyl steroid dehydrogenase, it increases excess of cortisol to mineralocorticoid receptors causing sodium retention and potassium depletion, so it may interfere with various medicines including antihypertensive and antiarrhythmic agents. A high intake of liquorice can cause hypermineralocorticoidism with sodium retention and potassium loss, oedema, increased blood pressure and depression of the renin-angiotensin-aldosterone system. Studies showed that a daily consumption of glycyrrhizic acid of 95 mg or more caused an increase in blood pressure. A practical guideline for an acceptable daily intake of glycyrrhizic acid seems to be 9.5 mg a day. This means no more than 10-30g liquorice and no more than half a cup of liquorice tea a day.

Antibiotics are widely prescribed in medical practice. Many of them induce or are subject to interactions that may diminish their anti-infectious efficiency or elicit toxic effects. Food intake can influence the effectiveness of an antibiotic. Avoid co-administration of antibiotics with milk products which are rich sources of divalent ions, such as calcium and magnesium that complex with some antibiotics and prevent their absorption. The intake of dairy products, however, needs to be monitored and encouraged with appropriate consideration of specific antibiotics involved.

A number of studies give evidence that fluoroquinolones forming slightly soluble complex with metal ions of food show reduced bioavailability. Casein and calcium present in milk decrease the absorption of ciprofloxacin. The effect of interaction of five fruit juices on the dissolution and absorption profiles of ciprofloxacin tablets were determined. It was found that the absorption of ciprofloxacin (500 mg) tablets can be reduced by concomitant ingestion of the GFJ. Therefore, to avoid drug therapeutic failures and subsequent bacterial resistance as a result of sub-therapeutic level of the drug in the systemic circulation, ingestion of the juice with ciprofloxacin should be discouraged. Azithromycin absorption is decreased when taken with food, resulting in a 43% reduction in bioavailability. Tetracycline should be taken one hour before or two hours after meals, and not taken with milk because it binds calcium and iron, forming insoluble chelates, and influencing its bioavailability.

Analgesics and antipyretics are used to treat mild to moderate pain and fever. For rapid relief, acetaminophen should be taken in an empty stomach because food may slow the body absorption of acetaminophen. Co-administration of acetaminophen with pectin delays its absorption and onset. NSAIDs like ibuprofen, naproxen, ketoprofen and others can cause stomach irritation and thus they should be taken with food or milk. Avoid or limit the use of alcohol because chronic alcohol use can increase the risk of liver damage or stomach bleeding. The absorption of ibuprofen and oxycodone when given in the combination tablet was affected by the concomitant ingestion of food.

Bronchodilators like theophylline, albuterol, and epinephrine possess different effects with food. The effect of food on theophylline medications can vary widely. High-fat meals may increase the amount of theophylline in the body, while high-carbohydrate meals may decrease it. Avoid alcohol if taking theophylline medications because it can increase the risk of side effects such as nausea, vomiting, headache and irritability. Avoid eating or drinking large amounts of foods and beverages that contain caffeine (e.g., chocolate, colas, coffee, and tea) since theophylline is a xanthine derivative and these substances also contain xanthine. Hence consuming large amounts of these substances while taking theophylline, increases the risk of drug toxicity. Additionally, both oral bronchodilators and caffeine stimulate the central nervous system. Patients may be advised not to consume Grape Fruit Juice when taking theophylline, since it increases the bioavailability, and monitoring of plasma theophylline levels in patients consuming GFJ might be helpful in better management of patient care.

Fexofenadine, loratadine, rupatadine, cimetidine cetirizine, are all antihistamines. It is best to take prescription antihistamines on an empty stomach to increase their effectiveness. Rupatadine is commonly used for the management of diseases with allergic inflammatory conditions. A study indicates that concomitant intake of food with a single 20 mg oral dose of rupatadine exhibits a significant increase in rupatadine bioavailability. Cimetidine is given with food to assist the maintenance of a therapeutic blood concentration. A fraction of cimetidine is absorbed in the presence of food, allowing the remaining drug to be dissolved once the gut is cleared. Thus, therapeutic levels are maintained throughout the dosing interval.

Anti-tubercular drugs like isoniazid have been associated with tyramine and histamine interactions. Inhibition of monoamine oxidase and histaminase by isoniazid can cause significant drug-food interactions. Food greatly decreases isoniazid bioavailability. Oleanolic acid, a triterpenoid exists widely in food, medicinal herbs and other plants, has antimycobacterial activity against the *Mycobacterium tuberculosis*, when administered with isoniazid, it exerts synergistic effect.

High fat meals decrease the serum concentration of cycloserine, a bacteriostatic anti-tubercular drug and results in incomplete eradication of bacteria.

Glimepiride is an antidiabetic and a new generation sulfonylurea derivative should be administered with breakfast or the first main meal of the day. It has absolute bioavailability and the absence of food interaction guarantee highly reproducible pharmacokinetics. Immediate release glipizide should be taken 30 minutes before meals. However, extended release tablets should be taken with breakfast. The maximum effectiveness of acarbose, an alpha-glucosidase inhibitor is attained when the drug is taken immediately at the start of each meal (not half an hour before or after), because it delays the carbohydrate absorption by inhibiting the enzyme alpha-glucosidase.

Mercaptopurine is a purine analog used for acute lymphoblastic leukemia and chronic myelogenous leukemias. Since it is inactivated by xanthine oxidase (XO), concurrent intake of substances containing XO may potentially reduce bioavailability of mercaptopurine. Cow's milk is known to contain a high level of XO. This interaction may be clinically significant. Therefore most patients should try to separate the timing of taking mercaptopurine and drinking milk.

Tamoxifen is a successful anti-tumor agent. If taken with sesame seeds, it negatively interferes with tamoxifen in inducing regression of established MCF-7 tumor size but beneficially interacts with tamoxifen on bone in ovariectomized athymic mice. Xue et al. had compared the influence of dietary elements on cancer progression, chemotherapy efficacy, and toxicity, particularly severe, late onset diarrhea related to irinotecan (CPT-11) treatment. They suggest that glutamine and n-3 fatty acids might be potentially useful adjuncts with CPT-11 treatment.

Food-drug interactions can produce negative effects in safety and efficacy of drug therapy, as well in the nutritional status of the patient. drug interactions are to be avoided, due to the possibility of poor or unexpected outcomes. Like food, drugs taken by mouth must be absorbed through the lining of the stomach or the small intestine. Consequently, the presence of food in the digestive tract may reduce absorption of a drug. Like drugs, foods are not tested as comprehensively so they may interact with prescription or over-the-counter drugs

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CARBON DIOXIDE: CAPTURE AND UTILIZATION

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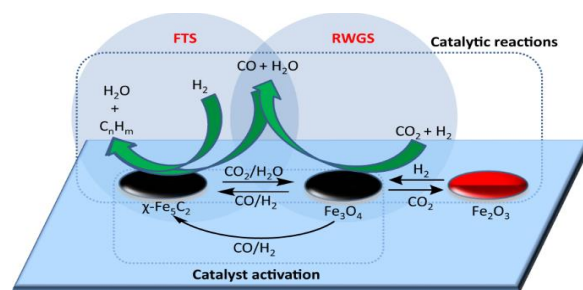
INTRODUCTION

Carbon dioxide is an important atmospheric constituent on the earth and plays an important role in many processes such as photosynthesis and respiration. To attain and maintain environmental stability and sustainability, the amount of carbon dioxide produced and consumed in the atmosphere should be balanced. Unfortunately, human activities such as burning of fossil fuels, transportation, industrial manufacture, deforestation and other human activities become a major cause for the enhancement of the amount of carbon dioxide in atmosphere drastically. Such activities if uncontrolled will significantly disrupt the carbon cycle on earth. Fossil fuels and biomass are the most common feedstock for the production of liquid fuels. Burning of these feedstock results in increase in carbon dioxide emission into atmosphere, hence it is necessary to develop strategies for upgrading this gas into useful products. With the rapid increase the carbon dioxide concentration in atmosphere, growing attention has received on global green house gas effect which causing climate change and rising sea levels. Among strategies for controlling carbon dioxide emission, the conversion of carbon dioxide into valuable chemicals has been recognized as the most long term and economic technology of utilizing carbon dioxide since it enable to produce high energy density carbon fuels.

In this chapter, different strategies for conversion of carbon dioxide in to valuable fuels were summarized and discussed with detailed comments of advantages and disadvantages.

METHODS FOR THE CONVERSION OF CO₂ IN TO FUELS

1. Catalytic Reduction of CO₂



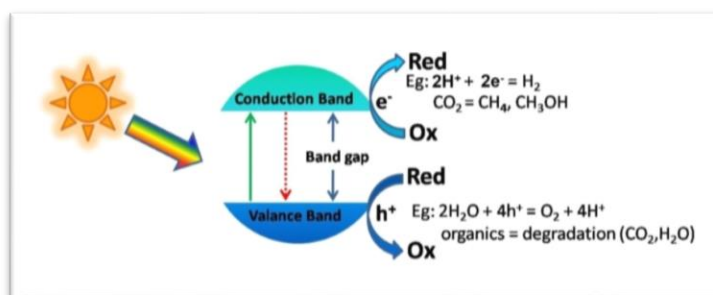
Synthesis of liquid fuel using CO₂ and H₂ is promising for the sustainability of mankind. The reported technologies usually proceed via CO intermediate, which needs high temperature, and tend to cause low selectivity. Direct hydrogenation of CO₂ to liquid fuel, not via CO, is a challenging issue. The reaction could proceed at 200 °C, which is much lower than those reported so far. Hydrogenation of CO₂ to liquid hydrocarbons usually proceeds through tandem catalysis of reverse water gas shift (RWGS) reaction to produce CO, and

subsequent CO hydrogenation to hydrocarbons via Fischer–Tropsch synthesis (FTS). RWGS reaction is endothermic and needs a higher temperature, whereas FTS reaction is exothermic and is thermodynamically favoured at a lower temperature. There are two ways to convert CO₂ to liquid hydrocarbons; an indirect route, which converts CO₂ to CO or methanol and subsequently into liquid hydrocarbons, or the direct CO₂ hydrogenation route, which is usually described as a combination of the reduction of CO₂ to CO *via* the reverse water gas shift (RWGS) reaction and the subsequent hydrogenation of CO to long-chain hydrocarbons via Fischer-Tropsch synthesis. The key to advancing this process is to search for a highly efficient inexpensive catalyst, which can preferentially synthesise the target hydrocarbon range of interest. Iron-based catalysts, widely used in both the RWGS and FTS reactions, are typically prepared by chemical co-precipitation routes, which unfortunately consume significant amounts of water.

2. Photocatalysis

Solar energy is as an ideal energy source to replace traditional fossil fuels because it is an abundant, cheap, clean, and sustainable energy source. Therefore, the use of photocatalysts for solar-driven fuels from CO₂ is a very attractive approach. Similar to natural photosynthesis, electron–hole pairs are generated when the photocatalysts are exposed to solar light. The photogenerated electrons induce CO₂ to undergo a redox reaction that results in hydrocarbon formation.

There are three crucial procedures during the photocatalytic conversion of CO₂: Absorption of sunlight; Charge separation and transfer; and Catalytic reduction of CO₂ and oxidation of H₂O.



Each procedure during the conversion of CO₂ is closely related with the photocatalysts. Until now, the photocatalysts were mainly from semiconductor materials which are abundant on earth and easy to obtain. The integration of photocatalysts with metal–organic frameworks (MOFs) has been demonstrated to offer more adsorptive sites for CO₂ uptake because of their extreme larger surface area and microporous structure, resulting in remarkable improvement in CO₂ conversion. Integration of photocatalysts with metal–organic frameworks has been are provide more adsorptive sites for CO₂ uptake because of their extreme larger surface area and micro porous structure, resulting in remarkable improvement in CO₂ conversion.

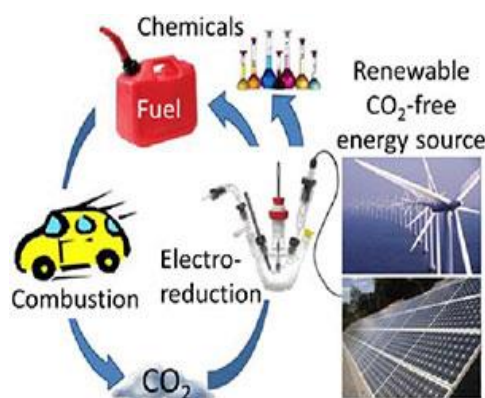
Two dimensional (2D) nanosheets are particularly promising in improving charge separation because the photo generated electrons and holes will move to the interface with shorter distances.

3. Electrocatalysis

The electrocatalytic conversion of CO₂ to valuable chemicals is an attractive solution for reducing atmospheric CO₂ and storing energy. Using an external electric field as an energy source and water as the proton donor, various catalysts are applied to catalyze the reduction of CO₂. The electrocatalytic conversion is a higher cost-effective method because water replacing H₂ is used as the proton donor. Electrocatalytic CO₂ reduction has attracted great attention due to its mild operating conditions (normal temperature and pressure),

controllable reaction process conditions and reaction rate, recyclable catalyst and electrolyte, high energy utilization, simple equipment, and achievable conversion efficiency. In the past few years, researchers have explored electrocatalytic reduction of CO₂ using different electrode materials, such as metals transition metal oxides, transition metal chalcogenides, metal-free 2D materials, metal-organic frameworks (MOFs), and various reduction products including CO, methane, formic acid, ethanol, and other compounds were obtained.

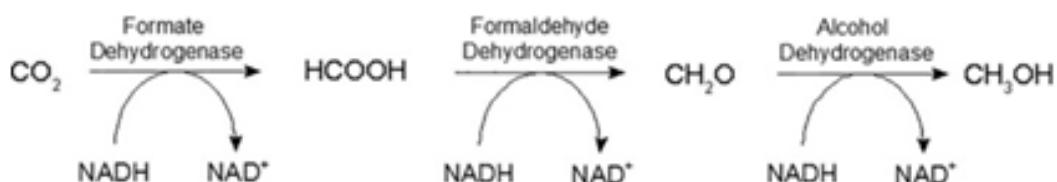
One of the factors that influence electrochemical reduction is the catalyst selection; therefore a catalyst that has a high catalytic activity and has selectivity towards methanol formation is required. Copper-based catalysts have been widely used in the electrochemical reduction of CO₂ to methanol; other metal catalysts have also been widely studied in recent years, including platinum catalysts as noble metals. Generally, electrochemical reduction is mostly carried out on bulk electrodes in electrolyte solutions, but it was found that limitations on mass transport and low solubility of CO₂ in electrolytes.



4. Enzyme Coupled to Photocatalysis

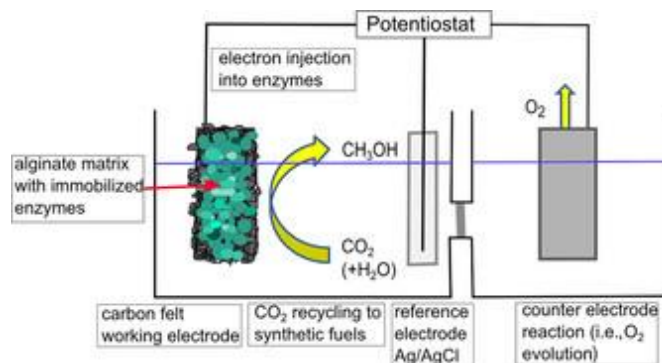
The reduction of CO₂ via biocatalytic processes received particular attention because of their special substrate and product selectivity as well as high conversion efficiency. Enzymes are biocatalysts renowned for their high efficiency and selectivity. In living cells, different enzymes often work together or in a specific order to catalyze multi-step biochemical reactions, playing crucial roles in the synthesis of natural products and metabolism. It is obvious that the research has presented an increasing tendency, especially in the recent 10 years, suggesting more and more attention was paid to the biocatalytic conversion of CO₂.

In general, to reduce CO₂ to methanol three enzymes, formate dehydrogenase (FateDH), formaldehyde dehydrogenase (FaldDH) and alcohol dehydrogenase (ADH), are required. In addition NADH is used as sacrificial coenzyme for the hydrogen and electron transfer. This means that for each reduction step one NADH molecule is irreversibly oxidized to NAD⁺ as depicted in the figure.



The photosynthesis that occurs in green plants and certain bacteria converts solar energy into chemical energy that can be well utilized by organisms and, at the same time, absorbs carbon dioxide and produces oxygen to maintain the carbon-oxygen cycle on the earth. This inspired people to explore the intrinsic mechanism of the photosynthesis process and to construct artificial analogues via bio mimetic mythologies for alternative sustainable energy carriers instead of traditional fossil fuels. In particular, photoreaction coupled with enzymes provides a highly efficient, specific, and energy saving strategy for CO₂ conversion and has attracted special attention in recent years.

Generally, enzymes are easily affected by the reaction environment, making the enzyme electrode unstable. For example, the enzyme cannot perform its maximum activity at a non-optimal pH solution. For the stability and reusability of the enzyme, appropriate fixation methods can be adopted.



CONCLUSIONS

This chapter summarizes the different methods for the conversion of carbon dioxide into fuels and valuable feed stocks. Catalytic hydrogenations, electromicrobial, electrochemical, photo electrochemical are various methods used for the conversion. Catalyst is a major component in all these methods. There are several routes for CO₂ reduction by H₂. CO production by RWGS can be used in downstream FT and MeOH synthesis, direct MeOH synthesis offers a liquid product with many application and finally CO₂. FT produces olefins and alkanes that can be used directly as fuels. Currently there is no preferred route for CO₂ hydrogenation by H₂ because the specific application ultimately dictates which route is the most attractive. Electrochemical methods are mainly attractive and effective because of superior in high efficiency, easy operation and various reaction pathways. Recent studies have reported the benefits of catalyst for CO₂ reduction and more researches will be carried out to improve its efficiency, develop new catalyst and reduce overpotential problem. The major obstacles are finding stable and low cost catalyst. Photoelectrochemical methods are preferred as it uses the easily available solar energy. There is a bright future in the reduction of carbon dioxide into valuable fuels. Cheap catalysts are developing and various researches are still going on in this field.

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SURFACE MODIFIED CATHODE MATERIALS FOR ADVANCED SOLID STATE BATTERY

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INTRODUCTION

In 1972, Sanyo introduced a battery on the market with materials Li for negative electrode and MnO₂ for the positive electrode. Moli energy developed the first rechargeable battery (secondary battery) in 1985. It is based on Li (anode) and molybdenum sulphide (cathode). But its design exhibited safety problems. Sony developed the first rechargeable Li-ion battery and introduced it on the market in 1991. Li-ion batteries are the most popular rechargeable batteries. In recent years, it has become an important power source and their performance gains are driving the adoption of electrical vehicles and grid storage. These are mainly used in cell phones due to low weight and high energy content(1). An ideal battery would possess properties such as long life, light weight, small size, high energy density, safety, low cost, environmental compatibility and worldwide consumer distribution. Most practical rechargeable batteries deliver capacities and energy densities below their theoretical values. Its efficiency may be enhanced by lowering the internal resistance of the battery, exhibit limited self-discharge. No memory effects that limit energy density after many cycle devices. In a Li-ion battery, Li⁺ is the guest ion and host network compounds are metal chalcogenides, transition metal oxides and poly anion compounds(2). These intercalation compounds can be divided into several crystal structures, such as layered, spinel, olivine and tavorite. The power and energy density of the LIB mainly depend on the electrode and electrolyte materials.

MATERIALS

Cathode: Cathode materials are detrimental to the performance and safety of Li-ion batteries. Most current intercalation cathode research is focused on the transition metal oxide and polyanion compounds due to their higher operating voltage and the resulting higher energy storage capability. Typically, intercalation cathode have 100-200mAh/g specific capacity and 3-5 average voltage vs. Li/Li⁺. The typical cathode materials of LIBs consist of layered lithium transition metal oxide LiMO₂ (M=Fe, Mn, Co, Ni, Ti, V etc..), Spinel lithium transition metal oxides, Polyanion compounds such as phosphates, silicates, fluorophosphates, flourosilicates, borates and graphitic materials such as graphene and graphene oxide(3).

Anode: The electrochemical performance, including cyclability, charging rate and energy density of Li ion batteries are significantly affected by anode materials. The typically used for fabricating the anode are metallic Li, graphitic carbon, hard carbon, synthetic graphite, lithium titanate, tin based alloys and Si based materials(4). The high capacity(3860mAh/g)

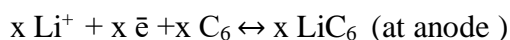
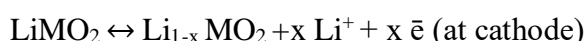
and lower potential of reduction of -3.04V vs primary reference electrode(SHE) make the anode metal Li as significant compared to other metal(5).

Electrolytes: Electrolytes must be carefully chosen to withstand the redox environment at both cathode and anode sides and the voltage range involved without decomposition or degradation. Electrolyte should be inert and stable in an acceptable temperature range. In commercial Li ion batteries, typically a liquid electrolyte is a solution of Li salts in organic solvents. However, the existing organic electrolytes can potentially catch fires under conditions of short circuit due to volatile and flammable nature of the solvents which are highly toxic. Various Li salts also used in including LiPF_6 , LiBF_4 , LiAsF_6 , LiClO_4 , and LiCF_3SO_3 (6). It should be care that anions are selected to avoid being oxidised on the charged surface of cathode.

WORKING PRINCIPLE

When a Li-ion based cell discharges, the Li^+ ions move from anode to cathode and reverse occurs on charging facilitated by a Li^+ containing salt in the electrolyte.

The reaction takes place here are:



The overall cell reaction is:



(M= transition metal)

An expanded view of LIB assembly is shown in **Figure 1**.

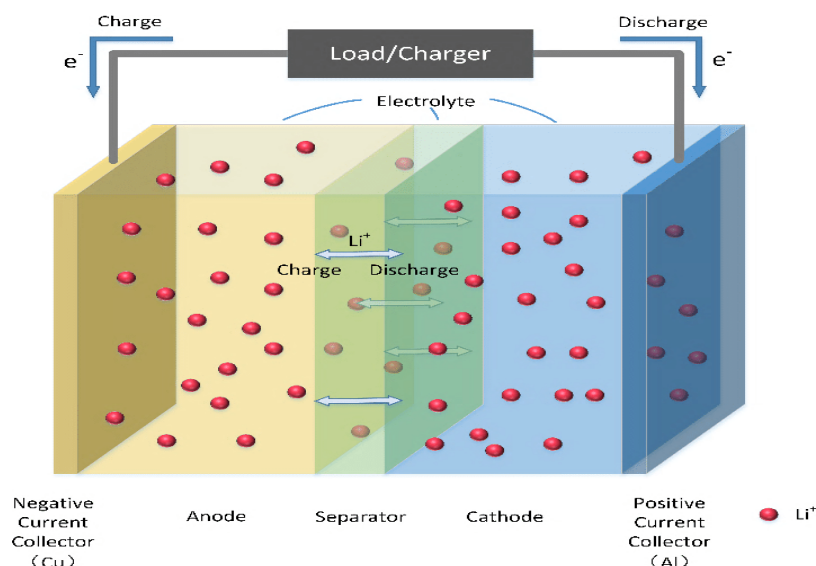


Figure 1. Schematic of Li ion battery

SOLID STATE BATTERY

Lithium-ion battery uses liquid electrolytes which are flammable and chance for explosion is high. John Goodenough invented solid state battery and won Nobel Prize in chemistry in 2019. Solid state batteries have found use in pacemakers, RFID and wearable devices. They are potentially safer with high energy densities, but at a much higher cost. They may avoid the use of dangerous or toxic materials found in commercial batteries. SSBs

are believed to have lower risk of catching fire and allow for faster charging. SSB, one of the best choices for the next generation of batteries, can serve as solid electrolytes materials with high conductivity (commonly referred to as super ionic conductors) but low electronic conductivity of 10^{-8}Scm^{-1} (7). Other features of an ideal electrolyte material for SSBs are:

- Wide electrochemical potential window.
- Good potential stability over the operating temperature range and toward the electrodes.
- Transference number of approximately 1.
- Matching thermal expansion coefficients with the cathode materials.
- Good chemical stability.
- Sintering temperature should match that of the electrode active materials.
- Low toxicity.
- Cost effective.

Compared to liquid electrolyte cells, most SSBs have high polarization, lower capacity, inferior power and cycling abilities which are attributed to increasing resistance at the cathode-electrolyte, electrolyte-electrolyte & anode-electrolyte interfaces(8). Common SSB architecture features a Li metal or composite particulate anode, a composite cathode and a solid state electrolyte membrane separating the electrodes. Compared to liquid state batteries solid state battery's energy density is high. In liquid electrolytes large separators are used between the liquid cells, whereas solid state battery requires very thin barriers to prevent short circuit. SSB can pack twice energy as Li-ion. A normal liquid electrolyte battery separator come with $20\mu\text{-}30\mu$ thickness whereas SSB can decrease the separator distance down to $3\text{-}4\mu$ (9).

Solid state batteries (**Figure 2**) can charge 6 times faster than liquid state batteries. In the case of life span, liquid electrolyte batteries need to replace after 3-5 years, but SSB last up to ten years and never explode catch fire if they are damaged or suffering from manufacturing defects; i.e., safer than LIB. SSB can operate -20°C to 60°C and their ionic conductivities greater than 10^{-2}scm^{-1} at 25°C .

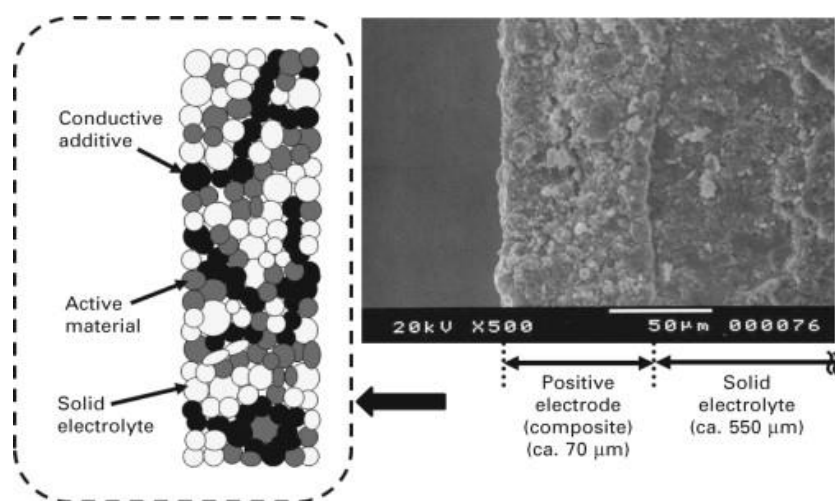


Figure 2. Cross-sectional SEM image of solid state battery

Compatibility between Cathode & Solid electrolyte: Solid state lithium batteries are widely accepted for next generation of various energy storage devices with the probability to realize improved energy density and superior safety performances. However there are many issues or challenges related to SSB, especially in the case of cathode and solid electrolyte. The development of the cathode materials for Li-ion batteries remains challenging because the existing materials such as layered transition metals oxides, olivines, or spinel all show upsides and downsides.

LiCoO₂ is well accepted material and it used for the commercial purpose. But it not absolutely trouble free and has disadvantages also.

Reaction between cathode & solid electrolyte: Interfacial chemical reaction stems from intrinsic chemical reactivity between the high-voltage cathodes and SSEs. These spontaneous reactions result in the formation of transition metal oxides, sulfides, phosphates and other undesirable products on the cathode–SSE interface that increase cell polarization and limit rate capability. Oxide anions from the layered transition metal oxides form stronger electrostatic attractions with lithium ions than sulfide anions due to the hard–soft acid–base principle(10). Thus, transfer of Li⁺ from sulfides to oxides occurs until equilibrium is reached, thickening the resistive layer and suppressing any ionic conduction across the interface.

Degradation: Degradation has a significant contribution to the performance decay of LiCoO₂. Bulk structure degradation of LiCoO₂ is the main reason for capacity loss at high voltage. The observations shows that by increasing the cutoff potential from 4.2 to 4.7 V, Li concentration was significantly decreased in the bulk. Besides, the samples with low Li content suffered from thermal instability when cycled to 4.7 V. There are uneven lithiation and de-lithiation behaviors in the bulk material. Besides structure degradation, interfacial degradation is one of the mechanisms assigned to the failure of layered cathode materials. It originates from the surface phase transformation layer and the cathode electrolyte interface (CEI) layer(11). The surface degradation is enhanced by increasing the cutoff potential.

Reorientation of crystal: During intercalation and deintercalation of Li for a large number of time, slowly the structure gets distorted and there is a change from the Rhombohedral symmetry to monoclinic symmetry, that become less symmetric, and this transformation reduces the intercalation capacity when charging and discharging occurs. i.e., energy rate or capacity gets decreased. Only 50% of theoretical capacity is realized due to structural instability. However it is much better compared to other rechargeable battery(12).

When commercial application is concerned high cost of cobalt and insufficient availability are very critical issues.

Formation of space charge layers: Space charge layers have detrimental effects on battery performance by increasing the resistance. A space charge layer formed when two materials with different chemical potentials are brought in contact with each other, and the atoms or electrons are unable to migrate to establish local charge neutrality.

Modifications: Interface compatibility has been a well known issue in the development of SSBs. Cathode coating is introduced to suppress undesirable interfacial reactions between cathode and solid electrolyte and prevented the diffusion of S ions from sulphide electrolyte to the oxide cathode. Moreover the electrochemical properties of all solid state cells were improved by cathode coating. Coated electrode presented better rate capability and lower interfacial impedance. Cathode coatings are used to isolate the SSEs from the low Li chemical potentials exerted by the cathode in its highly charged state, thereby preventing

their electrochemical self decomposition (13). By introducing a proper buffer layer effectively improves stability. A buffer layer has been used in the Li electrode to prevent the reduction of Ti^{4+} in NASICON-type solid electrolyte by metallic Li.

EXPERIMENTAL METHOD

Many attempts have been implemented to improve the cathode-electrolyte interface compatibilities. For example, Al_2O_3 layers on to $LiCoO_2$ (LCO) surface by ALD method and A solution based approach, where the LCO particles were coated with nanometer thick $Li-LiSnS_4$. However these are fail to achieve long-life cycling performance and could not address the degeneration of connection during cycling respectively. Here we used a novel buffer layer design technology with comprising of the $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ [LATP] solid electrolyte and the mixed ionic or semi-electric conductivity Li-ion intercalation compounds, which intimately improves the compatibilities at solid state interfaces. The solid state battery with the architecture of artificial buffer layer exhibits the stable and efficient cycling with a high reversible capacity at a rate of C/10 (LCO cathode~150 mAh/g and LFP~155 mAh/g).

Preparation of LATP: The $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ ($0 \leq x \leq 0.5$, especially $x = 0.3$, LATP) SEs were synthesized via a modified sol-gel method. The starting materials were $LiNO_3$ (99%, Alfa Aesar), $AlNO_3 \cdot 9H_2O$ (AR, Sigma aldrich), $C_{12}H_{28}O_4Ti$ (98%, Sigma Aldrich), and H_3PO_4 (85%, Sigma Aldrich). Stoichiometric amounts of the first three chemicals were dissolved in anhydrous ethanol, and 10 % excess $LiNO_3$ was added to compensate for Li volatilization during the high temperature preparation. And ~ 2% excess phosphoric was added to the solution. The solution evaporated at $70^\circ C$ for 12 hours to produce the dry-gel and then was calcined at $300^\circ C$ and $800^\circ C$ for 3 and 2 hours to synthesize the LATP powders. The LATP powders were then uniaxially pressed into pellets under and sintered at $1000^\circ C$ for 2 hours. After that heat treatment, some surface conditioning protocols, including the dry polishing (DP), and second heat treatments, were employed to reduce the interfacial resistance as well as the removal of Li_2CO_3 and $LiOH$ speciation on the ceramic surface.

Preparation of electrode-LATP composites: Two kinds of electrode -LATP composites were synthesized via a modified sol-gel method. Stoichiometric amounts of the first three chemicals ($LiNO_3$ (99%, Sigma Aldrich), $AlNO_3 \cdot 9H_2O$ (AR, Sigma Aldrich), $C_{12}H_{28}O_4Ti$ (98%, Sigma Aldrich)) were dissolved in anhydrous ethanol, and 10% excess $LiNO_3$ was added. Before adding of phosphoric acid (H_3PO_4 (85%, JK chemical)), an electrode material (NCM 811 (Arfwd Energy) or NCM 622 (Arfwd Energy)) with the mass ratio to LATP powders of 1:5 was added into the solution. After the electrode powders dispersed in the solution homogeneously, the phosphoric acid was added to the solution as the same amount of the LATP preparation process. The solution was evaporated at $70^\circ C$ for 12 hours to produce the dry-gel and then was calcined at the various temperatures in the range of $450-800^\circ C$ to get the electrode LATP composites.

Physical Characterization: The phase analysis was performed with a powder X-ray diffraction (XRD) (D2 PhaserBruker) (IIT Madras) using $Cu K\alpha$ radiation of $\lambda \sim 0.15418$ nm. The morphology of the powder samples was examined by a scanning electron microscope (SEM).

Preparation of composite cathode: NCM811 ($LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$) as cathode material was selected for the experiments. Firstly, the electrode material, carbon black, and binder PVDF were mixed in a 7:2:1 mass ratio. The homogeneously mixed slurry was done in a mortar for 30 minutes. Then the N-Methyl pyrrolidone (NMP) was added as solvent in the mixed powders, and the mixture was continuously mixed for another 20 minutes. The resultant slurry was spread onto the Al foil. After drying, those sheets were clipped into pellets with 12

mm in diameter as pristine electrodes. Then, the electrode-LATP composites, and PVDF were mixed in an 8:2 mass ratio to coat onto the as prepared electrodes as the composite buffer. Thirdly, following the same process, the LATP powders, and PVDF were mixed with NMP as solvent to coat onto the dried composite buffer layers. Subsequently, those dried as-prepared composite cathodes were uniaxially pressed under to ensure the dense interface contacts. After all these procedures, the composite electrodes were put into a vacuum oven at 100°C for 24 hours to evaporate the residual NMP and the water absorbed during the preparation.

To prepare the solid -state batteries with the composite cathode, we employed Li metal as anode. Note that in this work the interfacial modification was focused on the cathode and solid -state electrolyte interface. Thus, the reduction of Ti^{4+} in LATP due to the presence of lithium anode was avoided by a separator which has no effect on investigation of the buffer layer between cathode and solid -state electrolyte. The charge -discharge tests were measured in a voltage range of 2.5 to 4.3 V composite cathode, respectively. The above prepared solid batteries were tested under a rate of C/10 at room temperature (NEWARE test station, Shenzhen).

RESULTS AND DISCUSSION

Structural investigation: Figure 3 shows results of the X-ray diffraction analysis of both the initial materials (cathode material NCM and solid electrolyte LATP). All the diffraction peaks of NCM can be indexed as hexagonal layered α - $NaFeO_2$ -type structure (space group R3m) as evidenced by the distinct well-defined peak splitting (006)/(102). X-ray patterns of the samples with the protective interface layer of LATP do not reveal either impurity peaks or peaks of the initial LATP material, which could be related to its negligible amount.

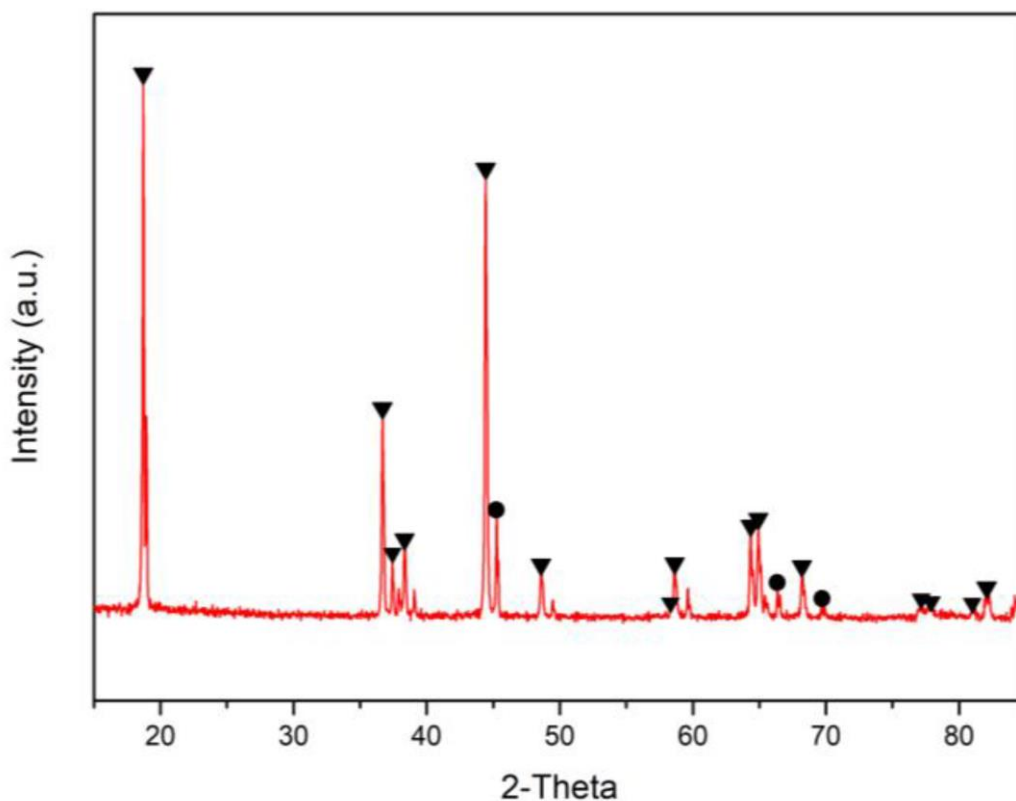


Figure 3. X-ray diffraction analysis

LATP Coated Cathode

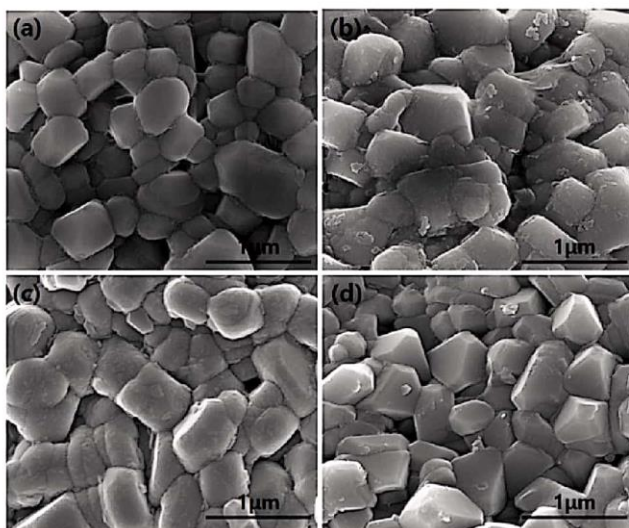


Figure (a): Uncoated cathode
 Figure (b), (c), (d) all LATP coated cathode materials

Morphology Analysis: Figure 4 shows the SEM images of pristine and LATP-coated sample with the 1% LATP. The spherical particle size of LATP-coated NCM is around 10 μm , similar with pristine sample, and the spherical secondary particles (10 μm) consist of primary particles with sizes of $\sim 500\text{ nm} - 1\ \mu\text{m}$.

LATP Coated Cathode

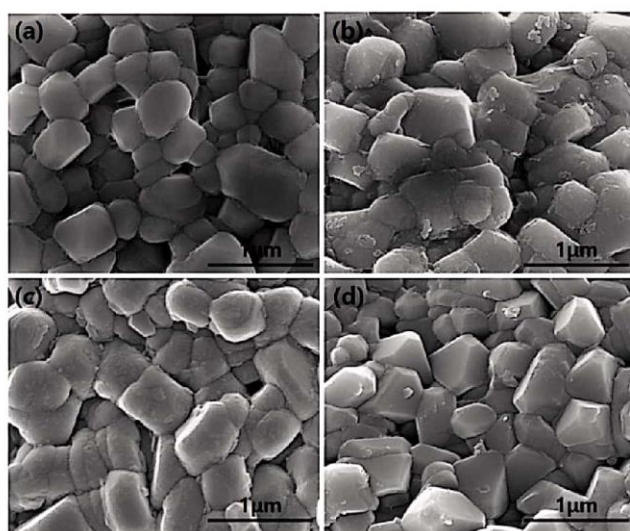


Figure (a): Uncoated cathode
 Figure (b), (c), (d) all LATP coated cathode materials

Figure 4. SEM Image of pristine and LATP coated sample with 1%LATP

Charge-discharge characteristics

Charge/discharge curves for the NCM-811 with LATP coating and without coating over the 2.7–4.2 V potential range and at a C rate of 0.1C. The initial NMC sample has a discharge capacity of 144 mAh/g, which is lower than that of the LATP samples. For the composite materials with a protective interface layer base on 1% LATP, the discharge capacity decreased from increased from 144 to 200 mAh/g .

The influence of LATP on electrochemical characteristics of NMC was studied by cycling the cells over 0.5C/1.0 C for 50 cycles. Figure 6 shows the cycle data for the LATP coated and non-coated samples. Introduction of the solid electrolyte to the surface of the cathode materials reduced the reactivity between solid electrolyte and cathode materials.

According to **Figure 5** and **Figure 6**, the solid electrolyte has a stabilizing effect on the cathode. Yet further studies of the composite cathode material based on the core/shell structures are necessary to eliminate the effect of decreasing specific capacity of the active material when introducing the LATP solid electrolyte and to improve its protective properties by providing more efficient coating of the cathode material particles.

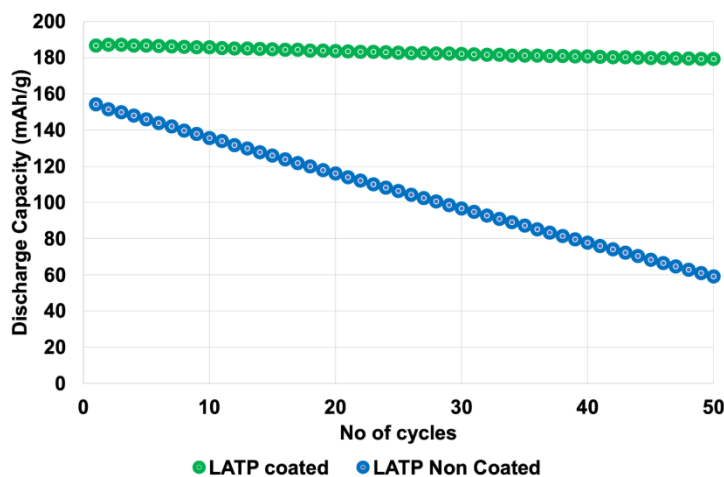


Figure 5. Charge/discharge curves for the NCM 811 with LATP coating and without coating

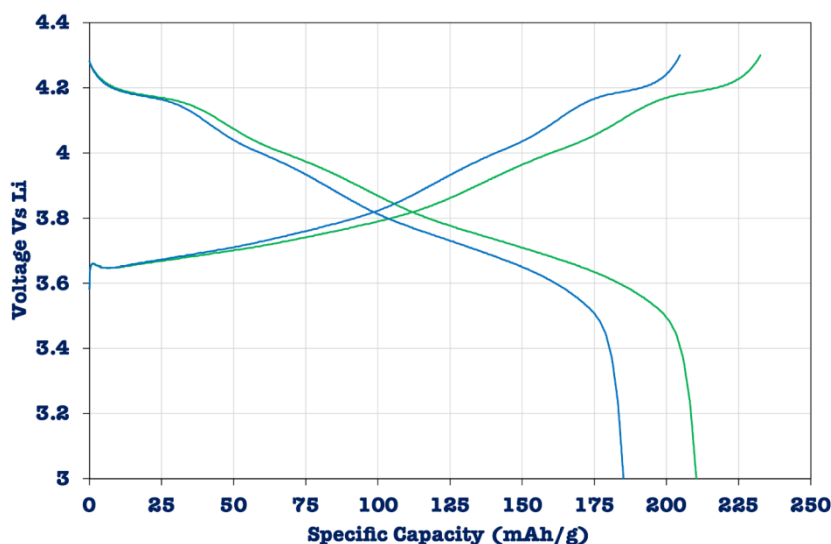


Figure 6. Cycle data for LATP coated and non-coated samples

CONCLUSIONS

Composite materials based on the NMC cathode material and protective layer of fine ceramic LATP electrolyte with a different LATP content (1%) have been studied. Synthesis of the composite materials improves electrochemical behavior of NMC, in particular its stability during cycling. Thus, coating the $\text{Li}_{1.3}\text{Ti}_{1.7}\text{Al}_{0.3}(\text{PO}_4)_3$ solid state electrolyte onto the $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ cathode material enables essentially improved stability of electrical characteristics of lithium ion batteries in long-duration cycling and decreased interfacial resistance between the active material and electrolyte in solid state batteries.

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SOURCES OF HEAVY METAL CONTAMINATION IN SOIL

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INTRODUCTION

Soils are the major sink for heavy metals released into the environment due to anthropogenic activities and unlike organic contaminants which are oxidized to carbon (IV) oxide by microbial action, most metals will not undergo microbial or chemical degradation. Heavy metals constitute a group of inorganic chemical hazards, and those most commonly found at contaminated sites are lead (Pb), chromium (Cr), arsenic (As), zinc (Zn), cadmium (Cd), copper (Cu), mercury (Hg), and nickel (Ni), and they persist in soil for a long time [1]. Biodegradation of organic contaminants in soil will be severely inhibited by the presence of toxic metals [2]. Heavy metal contamination of soil can cause risks and hazards to humans and the ecosystem by: direct ingestion or contact with contaminated soil, the food chain (soil-plant-human or soil-plant-animal-human), drinking of contaminated ground water, reduction in food quality via phytotoxicity, reduction in land usability for agricultural production causing food insecurity, and land tenure problems. Soils may become contaminated by the accumulation of heavy metals and metalloids from the rapidly expanding industrial areas, mine tailings, disposal of high metal wastes, leaded gasoline and paints, land application of fertilizers, animal manures, sewage sludge, pesticides, wastewater irrigation, coal combustion residues, spillage of petrochemicals, and air borne particulate matter.

Heavy metals occur naturally in the soil from the processes of weathering of parent materials at levels that are regarded as trace. Because of the disturbance and acceleration of nature's slowly occurring geochemical cycle of metals by man, most soils of rural and urban environments have been accumulated by one or more of the heavy metals in concentrations high enough to cause risks to human health, plants, animals, ecosystems, or other media [3]. A wide variety of anthropogenic sources of Metal-bearing solids in contaminated soils have been discussed hereunder.

FERTILIZERS

Agriculture was the first major human influence on the soil. To grow and complete the lifecycle, plants require not only macronutrients (N, P, K, S, Ca, and Mg), but also essential micronutrients. In some soils there will be deficiency in the heavy metals (such as Co, Cu, Fe, Mn, Mo, Ni, and Zn) that are essential for healthy plant growth [4], and crops have been supplied with these as an addition to the soil or as a foliar spray to provide adequate N, P, and K for crop growth. Large quantities of fertilizers are regularly added to soils in intensive farming systems. The compounds used to supply these contain trace amounts of heavy metals (e.g., Cd and Pb) as impurities, which, on continued fertilizer application can significantly increase their content in the soil. Cd and other potentially toxic elements including F, Hg, and Pb add to soil by application of certain phosphatic fertilizers.

PESTICIDES

Substantial concentrations of metals were found to be present in several common pesticides that are used fairly extensively in agriculture and horticulture in the past. Pesticides such as Bordeaux mixture (copper sulphate) and copper oxychloride are examples. Lead arsenate has been used in fruit orchards for many years to control some parasitic insects. Such contamination has the potential to cause problems, particularly when the sites are redeveloped for other agricultural or nonagricultural purposes. Compared with fertilizers, the use of pesticides has been more localized, being restricted to particular sites or crops [4].

BIOSOLIDS AND MANURES

The use of numerous biosolids (e.g., livestock manures, composts, and municipal sewage sludge) to land inadvertently leads to the accumulation of heavy metals such as As, Cd, Cr, Cu, Pb, Hg, Ni, Se, Mo, Zn, Tl, Sb etc. in the soil [5]. Although most manure are seen as valuable fertilizers, in the pig and poultry industry, the Cu and Zn added to diets as growth promoters and As contained in poultry health products also have the potential to cause metal contamination of the soil. When repeatedly applied to restricted areas of land, the manures produced from animals on such diets contain high concentrations of As, Cu, and Zn can cause considerable buildup of these metals in the soil. Biosolids (sewage sludge) are primarily organic solid products, produced by wastewater treatment plants that can be beneficially recycled [6]. Land application of biosolids materials is a common practice in many countries that allow the reuse of biosolids produced by urban populations. There is considerable interest in the use of composting biosolids with other organic materials such as sawdust, straw, or garden waste. If this continues, there will be implications for metal contamination of soils. The potential of biosolids in causing heavy metal contamination of soil has great concern about their application in agricultural practices. Common heavy metals found in biosolids are Pb, Ni, Cd, Cr, Cu, and Zn, and the metal concentrations are governed by the nature and the intensity of the industrial activity, as well as the type of process employed during the biosolids treatment.

WASTE WATER

The metal concentrations in wastewater effluents are usually relatively low but long-term irrigation of land with such can eventually result in heavy metal accumulation in the soil. The application of municipal and industrial wastewater and related effluents to agriculture land dates back 400 years and now is a common practice in many parts of the world [7]. Farmers were not bothered about environmental benefits or hazards and are primarily interested in maximizing their yields and profits.

METAL MINING, MILLING PROCESSES AND INDUSTRIAL WASTES

Mining and milling of metal ores coupled with industries in many countries responsible for the legacy of wide distribution of metal contaminants in soil. During mining, tailings (heavier and larger particles settled at the bottom of the flotation cell during mining) are directly discharged into natural depressions, including onsite wetlands resulting in higher concentrations of heavy metals [8]. Extensive Pb and zinc Zn ore mining and smelting have been resulted in contamination of soil that poses risk to human and ecological health. Soil heavy metal environmental risk to humans is generally related to bioavailability. Assimilation of heavy metal pathways include the ingestion of plant material grown in (food chain), or the direct ingestion (oral bioavailability) of, contaminated soil. Heavy metals are generated by a variety of industries such as textile, tanning, petrochemicals from accidental oil spills or

utilization of petroleum-based products, pesticides, and pharmaceutical facilities and are highly variable in composition.

AIR-BORNE SOURCES

The airborne sources of metals include stack or duct emissions of air, gas, or vapor streams, and fugitive emissions such as dust from storage areas or waste piles. Metals such as As, Cd, and Pb can also volatilize during high-temperature processing. These metals will be converted to oxides and condense as fine particulates unless a reducing atmosphere is maintained [9]. All solid particles in smoke from fires and in other emissions from factory chimneys are eventually deposited on land or sea and most forms of fossil fuels contain some heavy metals. This is, therefore, a form of contamination which has been continuing on a large scale since the industrial revolution began.

SOLID WASTE

Environmental contamination of soil by heavy metals due to solid waste mismanagement is a global issue. Open dumping and open burning are the main implemented waste treatment and final disposal systems, mainly adopted in low-income countries. Uncontrolled disposal will lead to serious heavy metals pollution occurring in the water, soil, and plants [10]. As a result of poor solid waste management, most of developing countries were becoming a dumping ground for electronic and other hazardous wastes containing lead, cadmium, mercury, cobalt, arsenic etc.

TRAFFIC

Recent years witnessed intensification of road traffic and, with it, the quantity of substances emitted by vehicles. Such emissions need to be monitored for public health purposes. The contribution of cars and road transports to the global emission of atmospheric pollutants is highly increasing. The vehicle's fuel considered as the main source of heavy metals pollution [11]. These metals are found in vehicle's fuel, catalytic converters, fuel tanks, tires and brake pads, engines and other vehicle components, as well as in road surface materials. Heavy metals are released in the form of air particulates in urban atmosphere as liquid or solid particles. The emitted particulates in urban are rich in potentially toxic heavy metals such as lead, cadmium, nickel, chromium and zinc which can be a genuine health hazard. Pollution with heavy metal have a fallout. Soil considers the primary recipient of these pollutants as they enter the plants and then the food chain large impact on the environment as road transports contaminate the atmosphere, water and soil near the highways.

CONCLUSION

Soil pollution with heavy metals draws a serious concern because of their detrimental effects on the living biota. The persistent and non-biodegradable nature of heavy metals eases their accumulation in the environment. Due to the increasing awareness among the public and the detrimental effects of these contaminants on human health, scientific communities are focusing on development of some new technologies for removal of these metals from contaminated soils.

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