Applications of Nanotechnology

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Preface

Nanotechnology, the manipulation of matter at the atomic and molecular scale, has emerged as a cornerstone of innovation in the 21st century. Nanotechnology has emerged as a transformative field with vast implications across various sectors, revolutionizing the way we interact with materials and processes on a molecular level. Its applications span a wide spectrum of industries, from agriculture to medicine, from energy to daily consumer products.

This book explores the diverse applications of Nanotechnology, focusing on its profound impact on agriculture, food production, environmental sustainability, medicine, energy solutions, and everyday life. As we delve into the chapters ahead, we uncover the transformative potential of nanomaterials in enhancing crop yields, preserving food quality, purifying our environment, revolutionizing medical treatments, powering sustainable energy solutions, and imbuing everyday life with novel functionalities. This book aims to provide a comprehensive overview of these diverse applications, shedding light on the remarkable advancements and future prospects in this rapidly evolving field

SHAMSHEERA K O

In memory of Korambayil Ahamed Haji Sahib

The founder, Korambayil Ahamed Haji Memorial Unity Women's College, and the visionary leader who could see beyond the current situation and imagine a better future which could inspired others to dream big and work hard to turn those dreams in to reality.

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Nanomaterials to Reduce Environmental Pollution

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Introduction

Nanomaterials, with their unique properties at the nanoscale, have emerged as promising tools to address and mitigate environmental pollution. These materials, typically sized between 1 and 100 nanometers, exhibit enhanced reactivity, surface area, and catalytic capabilities compared to their bulk counterparts. In the realm of pollution reduction, nanomaterials find applications in various environmental remediation strategies.

Firstly, nanomaterials are employed in advanced water treatment technologies, effectively removing pollutants such as heavy metals, organic contaminants, and microorganisms. Nanoparticles like graphene oxide, carbon nanotubes, and metal oxides display exceptional adsorption and catalytic properties, facilitating the purification of water sources.

Secondly, in air pollution control, nanomaterials play a crucial role in developing efficient catalytic converters for automobiles and industrial processes. Nano-sized catalysts enhance the conversion of harmful pollutants like nitrogen oxides and volatile organic compounds into less harmful substances, contributing to cleaner air quality.

Overall, the application of nanomaterials in environmental remediation showcases their potential to revolutionize pollution control by offering innovative and efficient solutions for cleaner water and air, paving the way for a more sustainable and ecologically balanced future [1].

Nanomaterials to Treat Polluted Water

Nanomaterials play a pivotal role in revolutionizing water treatment processes due to their unique physical and chemical properties. Their application in water treatment addresses challenges related to pollutants such as heavy metals, organic contaminants, and pathogens.

Adsorption: Nanoparticles like graphene oxide, carbon nanotubes, and metal oxide nanoparticles exhibit exceptional adsorption capacities. Their large surface area and high reactivity allow them to attract and capture pollutants from water. Functionalized nanomaterials can be tailored to selectively adsorb specific contaminants, providing a versatile and efficient method for water purification.

Catalysis: Nanomaterials act as catalysts to accelerate chemical reactions involved in water treatment. Metal and metal oxide nanoparticles, such as titanium dioxide and iron-based nanoparticles, can catalyze the degradation of organic pollutants and convert toxic substances into less harmful byproducts. This photocatalytic process is particularly effective in the presence of light, making it suitable for solar-driven water treatment applications.

Nanostructured Membranes: Nanomaterials are incorporated into membranes for filtration processes. Engineered nanomaterials, such as carbon nanotubes or nanofibers, enhance the permeability and selectivity of membranes, allowing for more efficient removal of contaminants. These membranes are used in various filtration techniques like ultrafiltration and nanofiltration.

Nano-Scale Filtration: Nanomaterials are employed in advanced filtration systems to remove nanoparticles and microorganisms. Silver nanoparticles, for instance, exhibit antimicrobial properties and can be integrated into filters to disinfect water by inhibiting the growth of bacteria and viruses [2].

Sensor Technologies: Nanomaterial-based sensors are utilized for real-time monitoring of water quality. Nanoparticles can be functionalized to selectively interact with specific contaminants, enabling the development of highly sensitive and selective sensors. These sensors provide rapid detection of pollutants, allowing for timely intervention in water treatment processes.

Remediation of Groundwater: Nanomaterials are applied in the remediation of groundwater contaminated with heavy metals or industrial pollutants. Nanoparticles, such as zero-valent iron, can be injected into the subsurface to facilitate the in-situ remediation of contaminants through processes like reduction and precipitation.

The integration of nanomaterials in water treatment processes offers a sustainable and efficient approach to address diverse water quality challenges, contributing to the provision of safe and clean water for various applications.

Nanomaterials to reduce Air pollution

Nanomaterials have shown significant potential in reducing air pollution through various innovative applications.

Catalytic Converters: Nanomaterials play a crucial role in catalytic converters for automobiles and industrial processes. Transition metal nanoparticles, such as platinum, palladium, and rhodium, supported on high-surface-area nanomaterials like zeolites or metal oxides, enhance the efficiency of catalytic reactions. These reactions convert harmful gases, such as nitrogen oxides (NOx) and carbon monoxide (CO), into less toxic substances, contributing to cleaner air quality [3].

Air Purification Filters: Nanomaterials are integrated into air purification filters to enhance their performance. Nanofibers, nanoparticles, or nanostructured materials with high surface areas are used to trap and remove particulate matter, allergens, and pollutants from the air. This technology improves the efficiency and longevity of air filters, ensuring better air quality in indoor and outdoor environments.

Photocatalysis: Nanomaterials with photocatalytic properties, such as titanium dioxide ($TiO2$) nanoparticles, are employed to break down pollutants when exposed to light. This process helps degrade volatile organic compounds (VOCs) and other airborne contaminants, contributing to the reduction of air pollution. Photocatalytic coatings on surfaces like roads or buildings can also assist in purifying the surrounding air.

Carbon Capture and Storage (CCS): Nanomaterials are explored for their potential in capturing and storing carbon dioxide ($CO2$) emissions from industrial processes. Functionalized nanomaterials, such as metal-organic frameworks (MOFs) or porous carbon nanomaterials, exhibit high adsorption capacities for $CO2$. Integrating these materials into CCS technologies can help mitigate greenhouse gas emissions and combat climate change.

Sensors for Air Quality Monitoring: Nanomaterial-based sensors are developed for real-time monitoring of air quality. Nanoparticles functionalized for specific pollutants can be incorporated into sensor devices, providing accurate and sensitive detection. These sensors enable early identification of pollution sources, allowing for prompt intervention and improved management of air quality.

Nanotechnology in Diesel Exhaust Treatment: Nanomaterials are utilized in diesel exhaust treatment systems to reduce emissions of particulate matter and NOx. Diesel particulate filters (DPF) containing nanocatalysts or nanofibers effectively trap and catalytically convert harmful diesel exhaust pollutants, contributing to cleaner emissions.

Smart Coatings for Building Materials: Nanomaterial-based coatings are applied to building materials to reduce air pollution. These coatings can neutralize pollutants, such as nitrogen oxides, when exposed to sunlight or ambient air. Incorporating these smart coatings into infrastructure can contribute to the overall reduction of urban air pollution.

The multifaceted applications of nanomaterials in addressing air pollution highlight their potential to enhance the efficiency of existing technologies and pave the way for innovative solutions in the quest for cleaner and healthier air.

Advantages of nanomaterials in pollution control over conventional materials

Nanomaterials offer several advantages over conventional materials in pollution control, owing to their unique properties at the nanoscale.

Enhanced Surface Area: Nanomaterials possess an exceptionally high surface area-to-volume ratio due to their small size. This characteristic increases the active sites available for reactions, making them more efficient in adsorption, catalysis, and other processes compared to conventional materials.

High Reactivity: The high surface area and unique reactivity of nanomaterials result in improved chemical and physical interactions with pollutants. This makes nanomaterials more effective in processes like catalysis, adsorption, and degradation of pollutants, leading to enhanced pollutant removal capabilities.

Selective Adsorption: Nanomaterials can be tailored and functionalized to selectively adsorb specific pollutants. This selectivity allows for targeted removal of contaminants from air or water, minimizing the impact on non-targeted species and reducing the generation of secondary pollutants.

Improved Catalytic Activity: Nanomaterials exhibit superior catalytic properties, enhancing the efficiency of catalytic converters in automobiles and industrial processes. This leads to more effective conversion of harmful pollutants into less toxic substances, contributing to cleaner air.

Nanofiltration and Membrane Technologies: Nanostructured membranes made from materials like carbon nanotubes or graphene oxide are employed in water treatment. These membranes exhibit improved permeability and selectivity, allowing for efficient removal of pollutants in processes like ultrafiltration and nanofiltration [4].

Photocatalysis for Air and Water Purification: Certain nanomaterials, like titanium dioxide nanoparticles, demonstrate photocatalytic activity when exposed to light. This property is harnessed for the degradation of organic pollutants and pathogens in both air and water, providing an energy-efficient and sustainable pollution control method.

Smart Coatings and Sensors: Nanomaterials can be incorporated into smart coatings for surfaces and sensor technologies for real-time monitoring. Smart coatings can neutralize pollutants, while nanomaterial-based sensors offer highly sensitive and selective detection of pollutants, enabling timely intervention and management.

Resource Efficiency: The use of nanomaterials often requires smaller quantities compared to conventional materials due to their high efficiency. This can lead to resource savings and reduced environmental impact during manufacturing and application.

Innovative Applications: Nanomaterials enable the development of novel pollution control strategies, such as the integration of nanocatalysts in diesel exhaust filters or the creation of nanocomposites for advanced water treatment techniques, showcasing their versatility and adaptability [5].

In summary, the advantages of nanomaterials in pollution control stem from their unique physical and chemical properties, allowing for more efficient, selective, and innovative approaches to address environmental challenges compared to traditional materials.

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Chapter 2

Nanomaterials: Revolutionizing Agriculture and Its Applications

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The field of synthesizing, characterizing, and applying nanoscale materials has seen remarkable technological advancements. Nanotechnology, with its interdisciplinary approach, has transformed science into a more application-oriented discipline. Nanomaterials, defined as materials with at least one dimension falling within the size range of 1 to 100 nm, exhibit distinct physico-chemical properties compared to bulk materials.

The imperative to address climate change, cope with population explosion, and meet the escalating demand for quality food and health necessitates the development of more advanced, dependable, and environmentally friendly technologies. This underscores the significance of the remarkable characteristics exhibited by materials at the nanoscale, where their properties are primarily determined by size and shape. The complexity of these materials' properties and their applications is further heightened by a multitude of surface functionalization opportunities. Consequently, nanomaterials have found applications in virtually every facet of life, including but not limited to medical fields, water and air purification, food production and enhancement, cosmetics, clothing, and various household products.

Nanotechnology and Agriculture

Agricultural products play a crucial role in our daily lives, serving as essential components in food, fuel, furniture, textiles, and feedstock. However, the productivity of agriculture faces significant challenges such as limited space, diseases, and shifts in agro-climatic conditions. The utilization of fertilizers and pesticides to improve crop yield has demonstrated adverse effects, some of which are severe and life-threatening. Consequently, there is an urgent need to modernize agricultural practices and methods, leveraging insights from cutting-edge technologies. This is where the relevance of applying nanotechnology in agriculture becomes evident. Emerging nanotechnological approaches show promise in enhancing agricultural productivity. These include the development of nano-formulations for agrochemicals to protect crops, the identification of toxicity using nanobiosensors, genetic manipulation of plants facilitated by nanodevices, and efficient diagnosis of plant diseases. Utilizing nanoarrays for the delivery of genetic material and proteins proves beneficial in crop engineering, drug delivery, and environmental monitoring. As we embrace these advancements, we pave the way for a more sustainable and effective future in agriculture. Nanotechnological methods have demonstrated significant applications in agriculture, encompassing fertilizer delivery, macronutrient supply, and insect pest management. Advances in nanoinsecticides, nanofungicides, and nanoherbicides further underscore its tremendous impact. Nanotechnology spans a wide spectrum in agriculture, ranging from biomass conversion technology and precision farming to alternative fertilizers. Its versatile applications extend from field-to-table processing of agricultural products, owing to the physiological influence of nanomaterials on plants, their role in pesticide bioremediation, smart packaging, and product tracking. Nanotechnology offers diverse agricultural solutions, including nano-sized nutrients, micronutrient fertilizers coated with zinc oxide nanoparticles, and nanoemulsions. The entry of harmful pesticides and herbicides into the food chain has heightened health concerns. Nanomaterial-based bioremediation presents a promising avenue to either completely degrade these compounds or convert them into non-toxic by-products. With a focus on health and environmental safety, nanotechnology emerges as a pivotal force in mitigating the adverse effects of current agricultural practices. The progress in bioremediation, encompassing substances like uranium, hydrocarbons, and soil contaminants, showcases its potential impact on soil remediation and groundwater safety. While the plant cell wall serves to impede the entry of external agents, nanoparticles possess the capacity to traverse through the pores. Engineered nanoparticles have been observed to induce the enlargement of existing pores or the formation of new pores during their uptake. Additionally, upon contact with the leaf surface, nanoparticles demonstrate absorption through stomata and trichome bases, subsequently undergoing translocation across the plant. Once internalized by the cells, the nanoparticles mediate their effect on the plant as a whole. Its functions can be determined by the particle size, shape, chemistry and surface functionalization.

Precision Farming and Nanotechnology

The application of nanotechnology in precision farming is anticipated to enhance agricultural yield while minimizing the use of chemical inputs. This approach aims to reduce the heavy accumulation of agrochemicals in soil and water. This involves the use of nanomaterials for the slow release of agrochemicals and managing plant diseases. Precision farming can be finely tuned by exploring the growth-regulating effects of nanomaterials, their application in soil water retention, and their role in delivering nutrients, thereby improving the quality of agricultural products. Nanotechnological methods, such as enhancing photosynthesis, food and biofuel production, and resistance to crop diseases, as well as nanobionics, show highly promising applications in agriculture. Exciting developments in plant nanobionics highlight the potential of biomimetic materials for light harvesting and biochemical detection. This approach holds promise for augmenting photosynthesis and biochemical sensing through the use of single-walled carbon nanotube–chloroplast assemblies. Advancements in nanofabrication and characterization methods have improved our understanding of the mechanisms of pathogenesis and enhanced strategies for disease treatment. Nanofabricated xylem vessels, mimicking capillary action, provide insights into the colonization, film development, and subsequent movement and recolonization at new sites by xylem-inhabiting bacteria. Intelligent nanosystems offer various advantages in agriculture, including the prevention of nutrient release into the soil, minimal leaching, improved uptake by plants, and mitigation of eutrophication.

Control Release Formulations

The process of nanoencapsulation involves coating the pesticide or active component with another material of varying size. This technique is employed for the controlled release of active ingredients, ensuring sustained activity over an extended period. Researchers have explored the potential of nanotechnology in mitigating the indiscriminate use of pesticides and promoting their safe application through nanoencapsulation. This approach facilitates a multistage delivery of pesticides, with slow release preventing premature degradation and enhancing efficacy for an extended duration. Consequently, it diminishes the quantitative need for pesticides, reduces human exposure, and proves to be more environmentally friendly compared to traditional applications.

Nanoagrochemicals

The enhancement of agricultural production through nanotechnology encompasses the utilization of nano-agrochemicals, the advancement of crop protection methods, and the effective post-harvest management of agricultural products. The production of polymeric nanoparticles that encapsulate herbicides provides an environmentally friendly approach to weed management. Additionally, the targeted application of herbicide-loaded nanoparticles directly to the roots of weeds facilitates effective weed removal. Various metal nanoparticles have also been employed as herbicides in commercial vegetable crops.

Nanopesticides

Nanoemulsions have been documented for their ability to encapsulate functional groups within droplets, thereby diminishing the quantity of necessary chemicals. The utilization of nano-sized materials enhances the stability of active compounds, concurrently reducing foliar leaching. Colloidal formulations of nanoinsecticides and pesticides exhibit noteworthy potential, notably diminishing chemical doses, frequency of applications, and, consequently, human exposure risk. To further enhance the environmental safety of nanoformulations, the incorporation of biocompatible and biodegradable polymers is recommended. Whether derived from petroleum or microbial sources, these biopolymers are environmentally degradable. Upon degradation, they release encapsulated active components.

Nanofungicides

The potential effectiveness of silver, carbon, silica, and alumino-silicate nanoparticles as antifungal agents has been investigated. Studies have reported the inhibition of various plant pathogens by silver and TiO_2 nanoparticles. Treatment with nanosilica has additionally demonstrated an increase in plant phenolic compounds, suggesting an enhancement in resistance.

Nanofertilizers

Various slow-release fertilizers (SRFs) and controlled-release fertilizers have been developed using synthetic or biopolymer materials. Additionally, polymeric nanoparticles have been employed as coatings for biofertilizers to enhance resistance to desiccation. Numerous nanomaterials have undergone extensive examination due to their properties as nanofertilizers. These encompass carbon-based nanoparticles, TiO_2, iron oxide, zinc oxide, and urea hydroxyapatite. The suggested benefits of their usage include improved nutrient mobilization, the preservation of soil health, and the promotion of microbial diversity, ultimately resulting in increased yields, nutrient-enriched food, and sustainability. Nano-sized materials have exhibited superior properties for promoting plant growth compared to bulk materials. This has been observed in the germination rate and germination vigor index of various plants, such as spinach. Additionally, applications of nanomaterials have been reported to enhance the photosynthetic rate, chlorophyll levels, plant dry weight, and seed stress resistance.

The integration of nanotechnology into agriculture encompasses several phases, including the synthesis of nanomaterials/nanofertilizers, nanoparticle delivery, the uptake and translocation of nanomaterials within plants, and their distribution. Although various methods of applying nanomaterials to plants have been demonstrated, foliar application has proven to exhibit superior performance. In the context of Vigna unguiculata, the positive impact of iron and magnesium nanomaterials on plant growth has been evident through foliar applications. Addressing the challenge of feeding a growing population necessitates enhancing agricultural productivity. The agriculture sector increasingly exploits the size and shape-based properties of nanomaterials. Despite being in its initial stages, the application of nanotechnology to agriculture holds the potential for the next agricultural revolution based on ongoing developments in this field.

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Chapter 3

Nanotechnology in Agriculture and Food

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1. Introduction

Nanotechnology has emerged as a transformative force across multiple domains. In agriculture, nanoparticles are revolutionizing crop production through enhanced nutrient uptake and controlled release of pesticides. Similarly, in food packaging, nanomaterials are extending shelf life and ensuring safety by creating barriers against moisture and pathogens. Across these sectors, nanotechnology is driving innovation, efficiency, and sustainability, promising a future where precision and effectiveness define our interactions with agriculture, food and healthcare.

2. Nanotechnology in agriculture

Over the past ten years, nanotechnology has brought about significant changes and cutting-edge advancements in agriculture. Notably, the use of nano-fertilizers has proven to be successful, improving nutrient efficiency in crops while reducing the reliance on chemical fertilizers. This not only boosts crop yields but also addresses concerns about fertilizer waste. Another milestone is the widespread adoption of nano-pesticides, which effectively reduce environmental pollution and minimize harm to ecosystems.

For instance, carbon nanotubes, a type of one-dimensional nanomaterial, have been found to enhance plant growth by improving nutrient usage efficiency. They are commonly used in pesticides and fertilizers after undergoing detailed characterization to ensure their safety. However, their potential cytotoxic effects need careful consideration before application. Studies have shown varying effects of carbon nanotubes on different aspects of cellular and microbial activity.[1]

Graphene, a representative two-dimensional nanomaterial, also shows promising effects in promoting plant growth and has been widely utilized in agriculture as both an insecticide and fertilizer. Like carbon nanotubes, graphene requires thorough characterization before use to understand its structural and chemical properties. Some studies have indicated adverse effects of graphene on plant growth and soil bacterial communities.

Metal oxide nanoparticles, such as mesoporous silica, have been extensively studied for their potential use in pesticides and fertilizers due to their ability to modulate nutrient release. However, high concentrations of these nanoparticles may have negative impacts on beneficial soil microbes.[3]

Furthermore, nanotechnology has revolutionized plant genetic improvement, allowing for precise editing and regulation of plant genes to enhance traits like disease resistance and drought tolerance. The integration of nano-sensors and monitoring technology enables real-time monitoring of soil quality, plant conditions, and weather patterns, leading to more efficient agricultural practices and reduced resource wastage, aligning with the goals of precision agriculture.

The advent of nanotechnology expands the possibilities of traditional agricultural practices, providing crops with increased adaptability to diverse environmental conditions, thereby enhancing resilience in agricultural systems. These innovations not only support increased food production and agricultural sustainability but also contribute to mitigating environmental impacts. They pave the way for the future of agriculture, playing a crucial role in ensuring global food security and promoting sustainable agricultural practices.[3]

3. NANO FERTILIZERS

3.1.Types of Nanofertilizers

Nano-fertilizers, emerging from advancements in nanotechnology, exhibit a variety of characteristics tailored to specific nutrient needs. They are typically categorized into two main types: macro-nutrient element nano-fertilizers and micro-nutrient element nano-fertilizers, based on the types of nutrients they provide. For macro-nutrient elements like nitrogen, phosphorus, and potassium, transforming them into nanoscale particles can alter their effectiveness and the way plants absorb them. For example, nano-nitrogen fertilizer can enhance the speed of nitrogen diffusion in soil, making it more effective and improving plant nitrogen absorption. By adjusting the pH of the soil microenvironment around roots, nano-fertilizers can enhance the absorption of these macro-nutrients. Micronutrients, crucial for crop disease resistance, can also benefit from nanoscale processing. Processing elements like boron and molybdenum at the nanoscale can enhance their solubility and availability in soil, leading to improved crop resilience.

There are two primary mechanisms of action for nano-fertilizers: first, nanomaterials that deliver nutrients to plants in nanoscale form to support growth and productivity, and second, engineered nanomaterials that enhance the efficiency of traditional fertilizers by acting as carriers for targeted delivery or release management.

The transport of nanoparticles within plants primarily occurs through two pathways: root uptake and foliar uptake. In root uptake, nano-fertilizers may penetrate root cell membranes, aided by translocation or ion channels. Factors such as ion concentration, soil pH, and temperature influence this process. In foliar uptake, nanoparticles may enter leaves through stomata or trichome roots or by penetrating leaf cell membranes, directly impacting physiological processes like photosynthesis. Deposition of nanoparticles on leaf surfaces can affect gas exchange by obstructing stomata, leading to alterations in plant physiology and cellular processes.

Overall, nano-fertilizers can be applied through root or foliar methods and are then transported to above-ground plant parts through the root system or leaf pores. Nanoparticles can directly penetrate plant cells if their sizes are smaller than cell membrane particles. Interaction with nanoparticles can interfere with metabolic activities and potentially enlarge or induce new cell wall pores, facilitating increased nanoparticle absorption.

The transport of silica nanoparticles in plants involves both extracellular and intracellular pathways, interacting with the root system and passing through various layers before entering the xylem.

Silica nanoparticles can also enter plants through stomata and be transported via the exosome route.

Various hypotheses have been proposed to explain the mechanisms of action, suggesting that irrigation is the optimal method for nanoparticle application if they enter plants through the xylem, while foliar spraying may prevent migration via the phloem.[2]

3.2.Nano-Nitrogen Fertilizer

The use of nano-nitrogen fertilizers offers significant benefits in improving nitrogen utilization efficiency [3]. Due to their small particle size, nano-nitrogen fertilizers bind more effectively to soil particles, extending the duration that nitrogen remains in the soil. This helps reduce nitrogen losses through volatilization and leaching. The precise release mechanism of nano-nitrogen fertilizers ensures that plants can efficiently uptake nitrogen during crucial growth stages thereby minimizing nitrogen wastage.

Moreover, the size advantage of nano-nitrogen fertilizers plays a crucial role in root interactions. Their smaller size allows for easier penetration of plant root systems, enhancing nitrogen uptake efficiency. This not only reduces the need for nitrogen fertilizers and increases nitrogen utilization by plants but also reduces environmental impacts, safeguarding agricultural productivity. Compared to traditional nitrogen fertilizers, nano-nitrogen fertilizers offer significant advantages in enhancing both crop yield and quality. The precise release mechanism of nano-nitrogen fertilizers ensures a consistent and steady nitrogen supply, maintaining stable nitrogen levels in crops throughout their growth cycle. This is expected to address concerns about nitrogen oversupply associated with conventional fertilizers, thus addressing environmental issues.[6]

Furthermore, the efficient uptake characteristics of nano-nitrogen fertilizers lead to improved nitrogen utilization by plants, resulting in enhanced growth and yield. This advancement offers more sustainable nitrogen management options for agricultural production, providing farmers with environmentally friendly choices. In conclusion, nano-nitrogen fertilizers demonstrate clear benefits in improving nitrogen utilization efficiency, reducing environmental pollution, and enhancing both crop yield and quality. These attributes present new possibilities for sustainable agricultural development.[1]

3.3.Nano Phosphate Fertilizer

Nano phosphorus fertilizers offer unique benefits in enhancing the effectiveness of phosphorus in soil. Their nanoscale particles possess a significant specific surface area, facilitating easy binding with soil particles to form a more stable complex. This process slows down the migration and leaching of phosphorus in the soil, thereby increasing its efficacy. Moreover, the nano-sized property enhances the interaction between the nano phosphorus fertilizer and the plant root system, improving phosphorus uptake efficiency by plants.

Nano phosphate fertilizers have a positive impact on promoting plant growth in agricultural production. By enhancing the effectiveness of phosphorus in soil, nano phosphorus fertilizers provide a more readily available nutrient source for plants, thereby accelerating the growth process. This growth promotion results in increased plant height, expanded leaf area, and a more developed root system, ultimately leading to higher yields. Importantly, this growth-promoting effect remains consistent across various soil types and climatic conditions.[3]

3.4.Nano Potassium Fertilizer

The application of potash nanoparticles has a significant impact on enhancing plant resilience. Nano-sized particles possess greater ability to penetrate the plant root system, leading to a more efficient delivery of potassium nutrients. This improvement helps strengthen plant resistance against various adverse conditions, including drought, salinity, and diseases. By enhancing the physiological activity and nutrient balance of the plant, potassium nano-fertilizers enhance its resilience to challenging environmental conditions, ultimately improving overall crop survival and yield.

Compared to traditional potash fertilizers, nano-potash fertilizers demonstrate more pronounced effects across diverse environmental conditions. A comprehensive understanding of the superiority of nano-potash fertilizers can be obtained by assessing their performance across different soil types, humidity levels, and temperatures. This comparative analysis is crucial in guiding farmers towards selecting the most suitable fertilizer options tailored to specific environmental conditions.[2]

4. Applications

The practical use of nano-fertilizers on major crops like rice and wheat presents compelling evidence. Implementations of nano-fertilizers have resulted in significant impacts on both yield and quality. For example, in rice cultivation, the application of nano-fertilizers has notably increased grain weight and improved overall grain quality

[58]. Assessing the sustainability of nano-fertilizers in agricultural systems requires long-term studies. These studies should not only assess yield performance within a single season but also track the effects of nano-fertilizers over multiple growing cycles. Observations over an extended period can provide a more comprehensive understanding of the potential long-term impacts of nano-fertilizers on soil quality, plant growth, and environmental considerations. Collectively, these application cases strongly support the adoption of nano-fertilizers in agriculture, contributing positively to increased crop yields, enhanced quality, and the promotion of agricultural sustainability.[4]

5. Nano-Pesticides

The integration of nanotechnology into pesticide applications offers innovative solutions for traditional agricultural practices. By incorporating nanotechnology into the pesticide formulation process, there is the potential to significantly improve pesticide effectiveness while simultaneously reducing adverse environmental impacts. Nano-pesticides are defined as formulations or products containing engineered nanoparticles with biocidal capabilities.

Nano-pesticides are available in various forms, including lipids, polymers, and metal-organic frameworks, each with different mechanisms for pesticide delivery and release. Polymer-based nano-pesticides may offer precise control over pesticide attachment and release on crop surfaces due to the tunability of their microstructures. Conversely, lipid-based nano-pesticides may enhance persistence and stability by allowing gradual pesticide release within the water column through the solubility of the lipid layer. Metal-organic frameworks, on the other hand, can facilitate efficient loading and gradual release of pesticides through their highly ordered pore structure. Many nano-pesticide compounds have demonstrated greater effectiveness compared to their commercial equivalents.[3]

6. Fundamentals of Nano-Pesticides

Nanotechnology plays a crucial role in formulating nano-pesticides by manipulating the particle size and structure of pesticides, often by encapsulating the active ingredient in nanoparticles. This approach enhances the stability and persistence of pesticides, extending their presence on plant surfaces. Such methods contribute to increased resistance against washout in adverse weather conditions, thereby enhancing their effectiveness. Some nanocarriers also exhibit responsiveness to environmental changes, offering improved targeting capabilities.

The unique properties of nanoparticles in pesticides provide distinct advantages for plant protection applications. The significant increase in surface area facilitates enhanced interaction between nano-pesticides and plant surfaces, improving adhesion effects. Moreover, the improved penetration ability of nanoparticles not only accelerates pesticide delivery but also allows for deeper penetration into plant tissues, resulting in more comprehensive control effects.

Through the application of nanotechnology, precise control over pesticide dosage becomes achievable, leading to reduced pesticide usage while maintaining efficient control. The heightened permeability and precise release mechanisms of nano-pesticides enable even relatively small doses to maximize their effects on plants. This contributes to minimizing the negative environmental impacts of pesticides, reducing costs in agricultural production, and enhancing control sustainability. These unique properties of nanoparticles form a robust foundation for optimizing the efficacy of pesticides.[3]

7. Pest Control Mechanisms

The mechanisms by which nano-pesticides affect pests are complex and diverse. Nano-pesticides, through their mesoporous properties, can create tiny traps on crop surfaces, increasing adsorption and attachment to pests. Modulating solubility may lead to a more gradual release of the pesticide within the pest, increasing its toxicity. The mode of release of active ingredients, such as the surface reactivity of nanocarriers, may allow pesticides to act in a more targeted manner on pest physiological systems, increasing their lethal effects. Smaller-sized nanoparticles exhibit enhanced penetration capabilities through both the epidermis and roots of plants, facilitating broader distribution of pesticides within the plant and thereby augmenting their efficacy against pests. The larger surface area of nanoparticles contributes to improved adhesion of pesticides to plant surfaces, extending their duration of action and reducing the necessity for frequent pesticide applications.[6]

Some nano-pesticides are specifically engineered for precise delivery to pest-affected areas through targeted delivery systems. This targeted approach minimizes the impact on non-target organisms while enhancing the pesticide's effectiveness.

The inherent properties of nanomaterials enable the design of systems for controlled pesticide release. For instance, responsiveness to environmental factors such as humidity, temperature, and pH allows for the regulation of pesticide release as required. This controlled release mechanism not only improves pesticide effectiveness but also reduces wastage, contributing to more sustainable and efficient pesticide applications.[3]

For example, silica nanoparticles are used as insecticides in two main ways: direct application of silica nanoparticles to crops to generate a silica coating that hinders insect and larval development and entrance, and the use of mesoporous silica nanoparticles to distribute commercial insecticides. Direct application is more lethal to adults and their larvae because silica has a drying effect. Silica nanoparticles also block the trachea or stomata of insects, which can be fatal to them.

8. Advantages of Nano-Pesticides

Nano-pesticides demonstrate superior environmental friendliness compared to conventional pesticides. Their small scale reduces the non-specific effects on beneficial insects and microorganisms, thereby improving crop protection. Additionally, nano-pesticides can precisely control pest and disease transmission while reducing the overall number of pesticides applied, thus enhancing utilization efficiency and reducing the risk of soil and water contamination. Nano-encapsulated pesticides offer various benefits such as controlled release kinetics, enhanced permeability, stability, and solubility, prolonged pesticide persistence, increased efficacy, and prevention of premature degradation of the active ingredient under stress conditions. These attributes potentially lead to improved pest control efficiency. Nano-pesticides have also been shown to significantly improve crop yields compared to conventional insecticides.

Furthermore, the use of chiral nanomaterials in nano-pesticides is a current research hotspot. They may efficiently control specific pests through chiral recognition and selective adsorption. Chiral nanomaterials offer superior biocompatibility, lower toxicity to non-target species, and better adherence to environmental friendliness and sustainability standards. In conclusion, the application of nanotechnology to pesticides is innovative, and ongoing research on nano-pesticides will continue to present opportunities for sustainable pest management and increased agricultural productivity.[3]

9. NANO TECHNOLOGY ON FOOD INDUSTRY

9.1.Nanoencapsulation

Nanoencapsulation in food involves the use of nanotechnology to encapsulate bioactive compounds, nutrients, or flavouring agents within nanoscale carriers such as liposomes, nanoparticles, or Nano emulsion. This technology offers several benefits, including protection of sensitive compounds from degradation during processing and storage, improved solubility and bioavailability, controlled release in the digestive system for enhanced absorption, and targeted delivery to specific tissues or cells in the body. Nanoencapsulation can be used to fortify foods with vitamins, minerals, or antioxidants, mask undesirable Flavors or Odors, and create functional foods with enhanced health benefits. However, regulatory considerations regarding safety and labelling of nonencapsulated ingredients remain important considerations in the food industry.

Encapsulation is an innovative technique involving the encasing of various active materials or bioactive components in solid, liquid, or gaseous states within matrices. This encapsulation enables the controlled delivery of these substances under specific conditions and at a specific rate. Bioactive ingredients like omega-3 fatty acids, curcumin, antioxidants, coenzyme Q10, carotenes, plant polyphenols, vitamins, growth promoters, herbicides, pesticides, among others, can be encapsulated into shells or nano capsules. This process serves to separate and preserve the active ingredients from the external environment, ensuring their stability and targeted delivery for enhanced efficacy. Nanoencapsulation improves biological efficiency and prevents side effects. It's widely used in food processing and preservation to extend the shelf life of products like meat, cheese, and beverages. For instance, in cured meat and sausage production, nanoencapsulation replaces traditional additives, enhancing taste and colour while reducing side effects.[4]

9.2.Nano Technology in Food Packing

Nanotechnology has brought significant advancements to food packaging, revolutionizing how we preserve and protect food products. Through the integration of nanocomposite materials, packaging barriers have been greatly improved, extending the shelf life of foods by effectively blocking out moisture, oxygen, and other gases. Additionally, active packaging solutions, incorporating nanoparticles loaded with antimicrobial agents, actively interact with food products to inhibit microbial growth, thus enhancing safety and freshness. Nano sensors embedded within packaging materials provide real-time monitoring of food quality indicators such as temperature and pH, ensuring optimal conditions and preventing spoilage. Smart packaging solutions utilize nanomaterials to respond to environmental changes or food deterioration, while nano-enabled traceability features offer transparency in the supply chain. Biodegradable nanomaterials, like nanocellulose, are also being explored to mitigate environmental impacts. With improved mechanical properties, nanotechnology enhances packaging durability and protection during transportation and storage. Overall, nanotechnology in food packaging holds immense promise for safer, longer-lasting products, though ensuring safety and regulatory oversight remains paramount.

Research in nanotechnology for food packaging has seen significant growth, with nanocomposite materials being a key focus. By incorporating nano-sized molecules into packaging materials, properties like toughness, mechanical strength, and thermal conductivity are enhanced. These nanocomposites typically consist of a polymer matrix with nano-sized particles distributed in either a continuous or discontinuous phase. Various types of nanoparticles, such as nanospheres, nanorods, and nanosheets, are utilized based on their specific characteristics. These nanocomposites improve mechanical strength and barrier properties, while also adding active or smart functionalities to the packaging system.

Nano-based food packaging offers numerous advantages over traditional methods, including better mechanical and physical barrier characteristics, antimicrobial properties, and nano-sensing for microbial detection. Nanofillers like TiO2 and clay enhance biopolymers, improving their mechanical strength and enabling additional functionalities such as oxygen scavenging and antimicrobial activity.

Studies show that blending halloysite nano clay with bovine gelatine polymer enhances properties more effectively than nano silica, leading to improved barrier qualities and water solubility. Overall, nanotechnology applications in the food industry enhance the quality, taste, texture, and nutrient bioavailability of food products. However, there are concerns about the potential transfer of nanoparticles from food packaging to the food itself, necessitating regulatory scrutiny to ensure safety and gain widespread acceptance in the food industry.[2]

9.3.Active Food Packaging

Active packaging in food technology involves packaging solutions that actively interact with the food or its environment to extend shelf life, enhance safety, or improve sensory attributes. This innovative approach goes beyond traditional packaging's role of containment and protection. Active packaging incorporates various agents such as oxygen scavengers, antimicrobial compounds, moisture absorbers, and ethylene scavengers. Oxygen scavengers remove oxygen from the package, delaying oxidation and food spoilage, while antimicrobial agents inhibit microbial growth to extend shelf life. Moisture absorbers maintain optimal moisture levels to prevent Mold growth and texture changes, and ethylene scavengers slow down the ripening process in fresh produce. Additionally, active packaging may include systems for flavour and aroma release or time-temperature indicators to assess freshness and safety. While offering benefits like improved food safety and reduced waste, it's crucial to ensure that active packaging materials comply with safety regulations and are suitable for food contact. The effectiveness of active packaging depends on various factors such as food type, packaging materials, and storage conditions.[4]

9.4.Antimicrobial Food Packaging

Antimicrobial packaging in nano food technology represents a cutting-edge approach to enhancing food safety and extending shelf life. By incorporating nanoparticles or nanostructures with antimicrobial properties into packaging materials, this technology effectively inhibits the growth of bacteria, fungi, and yeast that can cause food spoilage. Nanoparticles such as silver, zinc oxide, titanium dioxide, and copper are commonly used for their ability to release ions or molecules that disrupt microbial metabolism, preventing their proliferation. These nanoparticles can be integrated into packaging materials through various methods, including coating, blending, or embedding. Additionally, nanostructures can be engineered to possess surface properties that repel or kill microorganisms upon contact, ensuring the preservation of food quality. Furthermore, nano antimicrobial packaging offers selective action against harmful microorganisms while preserving beneficial ones, maintaining the natural microflora essential for flavour and nutritional quality. With excellent barrier properties against oxygen, moisture, and light, nano food packaging materials further contribute to extending the shelf life of food products. However, regulatory considerations regarding safety and potential nanoparticle migration into food necessitate continued research and oversight to ensure the effectiveness and safety of these innovative packaging solutions.[5]

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Chapter 4

APPLICATION OF NANOTECHNOLOGY IN THE FIELD OF MEDICINE & ENERGY

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1. INTRODUCTION

Nanotechnology plays a crucial role in both pharmaceuticals and solar energy. In drug delivery nanoparticles enhance drug specificity, reduce side effects and costs and improve solubility and patient comfort. Their versatility allows them to conjugate with diverse drugs, utilize ligands for cell-specific targeting, and employ co-polymers for immune protection. This multifaceted approach enhances precision and safety in drug delivery applications. The process involves receptor-mediated endocytosis, allowing controlled drug release for effective disease treatment. The chapter comprehensively explores nanotechnological applications across drug discovery, formulation, mechanisms, and real-world use. It provides valuable insights into the multifaceted aspects of utilizing nanoparticles for enhancing drug delivery and treatment effectiveness. The roadmap for nanotechnology for catalysis and solar energy conversion emphasizes leveraging nanotechnology for enhanced efficiency, durability, safety, and cost-effective production in renewable energy. Technologies like dye-sensitized, perovskite, and organic solar cells, along with innovations in quantum materials and nano-engineered electrodes, aim to boost solar-to-fuel conversion efficiency. Ongoing developments in perovskite and 'next-generation' solar cells, coupled with nanoscale analysis techniques and computational approaches, underscore the cutting-edge progress in renewable energy. Concepts like the 'electrochemical leaf' and biohybrid methods contribute to advancements in electrochemistry and enzyme-catalyzed efficiency, promising substantial societal benefits.

2. Nanotechnology in the Field of Drug Designing & Delivery

2.1. Introduction Nanoparticle Systems in Drug Delivery

Nanoparticles ranging from 100 to 500 nm offer opportunities for smart drug delivery. Manipulation of size, surface properties, and materials allows for targeted and controlled drug release. Nanotechnology has advanced cancer, AIDS, and diagnostic testing.[1]

2.2 Necessity for Nanoparticle-Based Drug Formulations.

Traditional drugs may not be optimally formulated for proteins or nucleic acids, necessitating innovative carrier systems. Nanoparticles enhance solubility, bioavailability, and targeted drug delivery, reducing toxicity and side effects. Development of new formulations drives pharmaceutical innovation and addresses patents and market forces [1,2].

2.3 Characteristics of Nanoparticle Drug Formulations

Particle size influences distribution, toxicity, and targeting ability. Hence nanoparticles under 200 nm preferred. Surface properties impact clearance and aggregation, with hydrophilic coatings enhancing circulation and reducing opsonization. Drug loading and release depend on factors like pH, temperature, and polymer type, affecting bioavailability and stability [1,2].

2.4 Targeted Drug Delivery

Nanoparticles can passively or actively target specific tissues, minimizing damage to healthy cells. Coating nanoparticles with targeting ligands enhances specificity and efficacy of drug delivery systems [1,3].

2.5 Surface Modification and Functionalization

Nanochemistry allows for the surface modification and functionalization of drug molecules and nanocarriers to improve their biocompatibility, target specificity, and cellular uptake. Surface engineering techniques such as ligand conjugation, PEGylation, or antibody targeting enable precise control over drug delivery and pharmacokinetics.[3]

2.6 Diagnostic and Therapeutic Nanosystems

Nanochemistry is instrumental in the development of multifunctional nanosystems for both diagnostic imaging and therapeutic applications. Nanoparticles functionalized with imaging agents (e.g., quantum dots, iron oxide nanoparticles) enable non-invasive imaging of diseased tissues, while simultaneously delivering therapeutic agents for targeted treatment [1,2].

2.7. Drug-Drug Interactions and Pharmacokinetics

Nanochemistry techniques are employed to study drug-drug interactions and pharmacokinetics at the nanoscale level, providing insights into the behaviour of drugs within biological systems. Understanding these interactions is crucial for optimizing drug combinations and dosing regimens to achieve desired therapeutic outcomes.[3]

3. Nanoparticles

There are mainly 2 types of nanoparticles as, Organic nanoparticles {Polymers in DDS (polymeric miscalls, polymeric NPs, polymeric drug conjugates), dendrimers, nano crystals and lipid-based NPs like liposomes, solid lipids} and Inorganic nanoparticles {Metal NPs (gold, silver, iron, platinum, quantum dots), Silica NPs (mesoporous, Xerogels)} [5,8].

3.1. Liposomes

Lipids, with both hydrophobic and hydrophilic parts, form lipid bilayers when in contact with water, creating spherical vesicles known as liposomes. They can carry both hydrophobic and hydrophilic drugs, improving drug solubility and pharmacokinetic properties while reducing side effects. Liposomes can be tailored in terms of shape, size, surface charge, and functional groups to suit specific drugs and target sites. Various methods are employed to prepare liposomes and incorporate drugs, controlling drug release through factors like pH and surrounding environment. Interaction with cells occurs through methods like adsorption, fusion, and endocytosis, enabling targeted delivery of drugs, including anticancer agents, neurotransmitters, and antibiotics. Surface modifications, such as using PEG, help overcome drawbacks like low encapsulation efficiency and rapid drug release, while also aiding in specific targeting for enhanced drug delivery efficiency [6].

3.2 Nano-Crystals

Nano Crystals are drugs produced in nano size, acting as their own carriers and readily soluble in water due to their size. They are stabilized by polymeric macromolecules and non-ionic surfactants, increasing their surface area and solubility. This leads to higher plasma concentration and reduced carrier particle accumulation. Polymeric nanoparticles, ranging from 10-100nm, use various synthetic or natural polymers and can be biodegradable or non-biodegradable. They incorporate drugs through covalent bonding, hydrophobic interactions, or water-filled pores, releasing them via diffusion, desorption, or erosion. These nanoparticles deliver drugs with minimal toxicity and undergo hydrolysis to produce biodegradable metabolites [6].

3.3 Polymer drug conjugates

Polymer drug conjugates involve proteins and peptides linked with polymers like polyethylene glycol (PEG) or PEG-camptothecin. These conjugates prevent protein drug degradation in the stomach, increase drug solubility in water, and extend drug half-life in plasma. Conjugated polymers evade recognition by white blood cells as foreign particles. Recent advancements include brush polymer drug conjugates synthesized via ring-opening metathesis copolymerization, which exhibit enhanced water solubility compared to traditional polymer drug conjugates [7].

3.4 Polymeric micelles

Polymeric micelles spontaneously form in aqueous solutions, consisting of amphiphilic surfactants arranged in a core-shell structure. The hydrophobic core accommodates poorly soluble drugs, while the hydrophilic shell stabilizes the core, prolongs circulation time and facilitates accumulation in tumors. Drugs can be incorporated through physical encapsulation or covalent attachment. For example, paclitaxel is incorporated into polymeric micelles for targeted chemotherapy in cancer treatment [7].

3.5 Dendrimers

Dendrimers are precisely structured synthetic polymers with sizes ranging from 1-10nm, composed of a core, dendrons, and surface-active groups. The chemical composition dictates biocompatibility and pharmacokinetics. They can encapsulate drugs within their core, controlling release rates. Dendrimers can be synthesized through divergent or convergent processes. Their cytotoxicity is influenced by core materials and surface nature. Drugs can attach to internal surfaces/core or dendrimer surfaces via covalent bonds, determining drug delivery specificity. For instance, methotrexate and doxorubicin can be delivered to tumors, while ibuprofen and piroxicam serve as anti-inflammatory drugs using dendrimers. Folic acid, antibiotics, cyclic targeting peptides, and PEG can enhance activity and specificity when attached to dendrimers [5].

3.6 Carbon nanomaterials

Carbon nanomaterials including nano-tubes (CNTs), C-60-fullerenes, and nano-horns (CNH), offer high electrical and thermal conductivity.

They are produced from graphite layers and can be single-walled or multi-walled. Surface modification with amphiphilic di-block copolymers, PEG, or hyaluronic acid enhances biocompatibility. Drugs can be attached via encapsulation, chemical adsorption, or functionalized CNTs. Controlled drug release is achieved electrically or chemically, protecting the drugs. CNH and C-60 fullerenes share similar properties. However, carbon nanoparticles may exhibit toxicity, influenced by geometrical structure and surface molecules like carbonyl and hydroxyl groups [6]

3.7 Silica Materials

Xerogels and mesoporous silica NPs have higher biocompatibility, convenient functionalization and high porous matrix. Xerogels has highly porous and surface area and drug loaded by sol-gel technique. The drug releasing rate can control by changing synthesis conditions such as temperature, pressure, ratio of reagents. Phenytoin, cisplatin, nifedipine, doxorubicin, matronidazole, heparin are drugs incorporated with xerogels. Mesoporous silica nanomaterials have high surface area for drug absorption, homogenous structure. Anticancer drugs, antibiotics, heart disease drugs are delivered by mesoporous and drug releasing controlled by diffusion method [9].

3.8 Metal nano-particles (MNP)

Gold, silver, iron, platinum, ceramic, quantum dots and super magnetic uses as NPs because of it shape depending optical, magnetic, electrical properties and size. Physical, chemical and green approaches uses to production of MNP’s. Physical methods are evaporation condensation and laser ablation. It provides less solvent contamination and uniform distribution. Chemical method uses reducing agents such as ascorbate, sodium borohydride, tollens reagent. Biological approach uses bacteria fungi and plant species for production MNM. Magnetic NPs can control with help of external magnetic field so it able to same time reported and treated diseases [10].

4. Application of Nanoparticle Technology in Pharmaceutical Therapy

Nanoparticles offer targeted drug delivery, reducing systemic toxicity in treatments.

- Micelles: They enable loading of water-insoluble drugs, enhancing stability and bioavailability while preventing interactions with serum proteins and non-target cells for targeted delivery. Combination with PEG copolymers in binary micelle systems improves drug loading, stability, and offers controlled release profiles. NK012, NK105, NK911, NC-6004, and SP1049C are micelles used for cancer therapy.
- Dendrimers: The unique structure and multiple surface groups they interact with proteins, facilitating intracellular uptake. Examples are polyamidoamine (PAMAM) dendrimers used for gene therapy and drug delivery to the central nervous system (CNS). Through stages of modification, dendrimers enhance biocompatibility, target the blood-brain barrier (BBB), facilitate drug delivery, and enable imaging for diagnosis.
- Nano emulsion: Nano emulsion formulations encapsulating poorly water-soluble drugs, such as curcumin or paclitaxel, improve their solubility and bioavailability when administered orally. These formulations enhance drug absorption in the gastrointestinal tract.

- Carbon nanotubes: Can carry water-insoluble drugs, functionalized for specific cancer receptors.

Interaction between CNTs and stem cells suggests potential for fabricating nervous tissue through cellular simulation for CNS disorders.

- Fullerene derivatives: Nano-C60 enhances cytotoxicity of chemotherapeutic agents.
- Liposomal nanoparticles loaded with chemotherapy drugs, such as Doxorubicin, are designed to specifically target cancer cells while sparing healthy tissues. This targeted delivery approach reduces systemic toxicity and enhances the effectiveness of the treatment.
- Nanogels: Nanogels demonstrate increased absorption of oligonucleotides in the brain while reducing absorption in the liver and spleen, making them promising transporters for drug delivery to the central nervous system (CNS). Nanogels-based formulation for methotrexate an anticancer drug.[10]

5. Nanotechnology for catalysis and solar energy conversion

The "Nanotechnology for Catalysis and Solar Energy Conversion" roadmap emphasizes leveraging nanotechnology to overcome existing energy conversion obstacles, highlighting the need for enhanced efficiency, durability, safety, and cost-effective, scalable production methods, as noted by Nathan Lewis. It concentrates on advancements in solar fuel generation, solar water splitting, photovoltaics, and bio-catalysis, incorporating technologies such as dye-sensitized, perovskite, and organic solar cells. Innovations in colloidal quantum materials and nano-engineered electrodes, as discussed by Waiskopf, Banin, and Meyer, are set to boost the efficiency of solar-to-fuel conversion. Furthermore, semiconductor nanoparticles are poised to enhance solar energy conversion rates, with Boschloo and colleagues showcasing this in dye-sensitized solar cells. Perovskite solar cells are also undergoing rapid development, with new research on 2D and 3D hybrid halides by Spanopoulos and others, while Nozik and Beard's work on 'next generation' solar cells introduces multiple exciton generation via hot carriers for significant photovoltaic efficiency gains through quantum effects in nanostructures. Overcoming these challenges necessitates advancements in nanoscale analysis, like the terahertz spectroscopy technique outlined by Milot and colleagues, which offers novel ways to characterize nanomaterials without the need for electrical contacts, facilitating in-operation device analysis and single nanoparticle assessment. Additionally, the field is seeing computational strides in predicting material and device properties, including machine learning applications for organic photovoltaics as discussed by Kohlstedt and Schatz. Megarity and Armstrong's 'electrochemical leaf' concept signals progress in electrochemistry, while biohybrid methods leverage precise enzyme catalysts for efficiency. These contributions underscore the cutting-edge nanotechnology and science driving renewable energy progress, poised to deliver substantial societal benefits.

5. 1. Colloidal quantum materials as photocatalysts for solar to fuel conversion

Over a decade ago, the potential of colloidal quantum materials, consisting of semiconductor nanoparticles, was recognized for their use as photocatalysts in converting solar energy into chemical energy. A key application of this technology has been in the area of water splitting, where the goal is to use the energy harnessed by these nanocrystals (NCs) to simultaneously produce hydrogen and oxygen gases through the reduction and oxidation of water, respectively. This process intriguingly sets the stage for a zero-emission cycle, where hydrogen gas could be combined with oxygen in a fuel cell to generate electricity, only to revert back to water.[11]

The customizable nature of these nanoparticles—through adjustments in size, shape, and composition—enhances their electronic band structures, maximizes their surface-to-volume ratio, and enables their direct use in solutions or embedded within matrices. This versatility has sparked extensive research into various water-splitting systems, which primarily focus on separating the two half-cell reactions to enhance efficiency. The tunability of these materials has also facilitated detailed studies aimed at uncovering the underlying factors that influence their performance and mechanisms.

The photocatalytic process involves several critical steps: light absorption, charge carrier mobility to the reaction site, and the catalytic reaction itself. Each step is influenced by a multitude of factors that need to be finely balanced to optimize the system’s overall efficiency. Key factors impacting these steps include the photocatalysts' composition and size, which dictate their electronic and chemical properties; the surface coating of the NCs, which must ensure dispersibility and passivation without hindering reactant access to the catalytic site; and the environmental conditions, which are crucial for maintaining chemical and colloidal stability while also affecting quantum yield.[13]

Addressing current and future challenges, the singular design of a homostructure NC falls short of meeting the comprehensive demands for effective photocatalytic water splitting. Hence, considerable efforts are directed towards creating integrated systems that combine multiple components to achieve synergistic effects, thereby meeting the requisite criteria for efficient solar-to-fuel conversion. Approaches such as semiconductor heterostructures, soluble cocatalysts, and semiconductor-metal hybrids have been explored to extend the absorption range, increase charge carrier lifetimes, and enhance the catalytic process. Additionally, innovative surface engineering techniques, including the attachment of molecular cocatalysts to nanoparticle surfaces, offer further possibilities to fine-tune nanoparticle properties for specific reactions.

Despite reaching new heights in achieving biocompatibility and high quantum yields, performance under mild conditions remains suboptimal. The longevity of these photocatalytic systems is also constrained by their chemical stability and the need for sacrificial additives in half-reactions. Expanding the lifespan of these systems, akin to their durability in display technologies, presents a significant challenge, with strategies like shell growth and ligand or polymer coatings being investigated to protect the NCs and facilitate charge carrier extraction. Future research is poised to explore systems capable of complete water splitting without sacrificial agents, enhancing both sustainability and efficiency.

In conclusion, colloidal quantum materials have demonstrated significant potential beyond their initial applications in light-emitting tags and display components. The complexity of their mechanisms in photocatalytic reactions invites continued exploration and innovation, particularly towards the goal of commercializing these materials for renewable, clean solar-to-fuel conversion processes.[12]

5.2. THz studies of nanomaterials for solar energy conversion

Terahertz (THz) spectroscopy represents a significant advancement in the characterization of nanomaterials, particularly for applications in solar energy conversion devices like solar cells and photocatalytic cells. This technique's ability to non-invasively probe the dynamic electrical properties of materials on ultrafast time scales is invaluable for optimizing the design and function of these devices. Here’s a simplified breakdown of the key points and their significance:

5.3. Understanding THz Spectroscopy

THz Range: THz radiation spans frequencies from 100 GHz to 10 THz, filling the gap between microwaves and infrared light. This range is particularly sensitive to fundamental charge processes in nanomaterials, making it a powerful tool for studying their electrical and dynamic properties.

-OPTPS Technique: Optical-pump-THz-probe spectroscopy (OPTPS) is a leading method in THz spectroscopy, utilizing femtosecond laser pulses to generate and detect THz pulses transmitted through or reflected from a sample. By altering the timing between these pulses, researchers can gather data on the photoconductivity and charge dynamics of nanomaterials.[13]

5.4. Applications in Solar Energy Conversion

-Charge Dynamics: Insights into photogenerated charge dynamics, such as charge separation, exciton formation, and recombination processes, are crucial for optimizing materials for solar energy conversion. THz spectroscopy provides a window into these ultrafast processes.

Metal Halide Perovskites (MHPs) THz studies have been instrumental in the rapid development of MHP solar cell materials, enabling precise measurements of charge mobilities, diffusion lengths, and recombination mechanisms.

-Semiconductor Nanowires and Nanoparticles for applications in photovoltaics and photocatalysis, understanding surface charge recombination and charge transport is vital. THz spectroscopy has revealed key properties that make materials like In-P nanowires suitable for these applications.[11]

5.5. Challenges and Future Directions

Data Processing and Modelling: Extracting meaningful electrical properties from THz spectra of nanomaterials is complex. The interaction of THz radiation with nanomaterials and their surrounding matrix requires sophisticated models to accurately interpret the data.

Industrial Application, Moving THz spectroscopy from a research tool to an industrial quality control method poses challenges in terms of measurement speed, reliability, and signal-to-noise ratio.

Single Nanoparticle Studies. There's a growing interest in applying THz spectroscopy to individual nanoparticles. Techniques like scattering near-field microscopy and THz-STM (scanning tunneling microscopy) are emerging, although they currently face significant challenges.

In summary, THz spectroscopy offers unparalleled insights into the charge dynamics of nanomaterials, essential for advancing solar energy conversion technologies. As researchers continue to refine this technique and overcome current challenges, it holds the promise of significantly impacting the development of next-generation solar cells and photocatalytic systems.

5.6. Surface-bound molecular assemblies on nanostructured electrodes for solar fuel generation

The potential and challenges of using solar energy for various chemical processes, specifically focusing on water splitting and CO2 reduction to produce hydrogen and other solar fuels. Here's a summary of the key points:

1. **Solar Energy as a Resource:** The Sun is a valuable but limited resource, available globally for only six hours a day.
2. **Photovoltaic Energy Schemes:** One way to utilize solar energy more broadly is through solar water splitting or the reduction of CO2 into solar fuels, using photovoltaic energy schemes.

3. **Photo electrochemical Cells**: These cells integrate water oxidation, and water or CO2 reduction, at separate semiconductor electrodes to capture and store solar energy as a translational energy source.
4. **Historical Development**: Experiments in this area began in the 1970s, with early work by Honda and Fujishima showing that UV excitation of nanoparticle TiO2 films in an electrochemical cell with a separate Pt electrode gave O2 and H2.
5. **Challenges**: Challenges in this area include the lack of molecular catalysts for water oxidation, issues with binding molecules to surfaces, and the need for stable surface molecular structures
6. **Research Contributions**: The passage highlights contributions from various researchers, including the demonstration of catalysts for water oxidation and reduction, as well as the identification of reductive catalysts for CO2 reduction.
7. **DSPEC:** The dye-sensitized photo-electro-synthesis cell (DSPEC) is described, which uses separate electrodes and nanoparticulate films for the two half reactions, employing chemical synthesis for the preparation and modification of chromophores and catalysts.
8. **Semiconductors**: TiO2 is mentioned as a key semiconductor for photoanodes, while NiO is noted for its potential as a photocathode despite challenges with injection efficiencies.
9. **Electrode Design**: Various electrode materials and designs are explored, including nanostructured tin-doped indium oxide (nanoITO), p-type Si, and p/n junction Si/GaN nanowire arrays.
10. **Surface Structure:** Stable surface structures are formed using phosphonate-derivatized chromophores and catalysts on oxide surfaces, stabilized by addition of metal oxide over layers.

11. **Chromophores:** A variety of chromophores have been explored for varying light absorptivity and excited state energetics, including polypyridyl complexes, porphyrins, and organic dyes.

12. **Recent Progress**: Recent research has focused on improving photocurrent efficiencies and stability, with promising results reported for Ru(II)bpy photoanodes and NiO-based photocathodes.

Overall, the passage highlights the significant progress made in utilizing solar energy for chemical processes, along with the ongoing challenges and areas of research focus in this field.[11]

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Chapter 5

Incorporation of Nanotech Breakthroughs in Daily Life

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Nanotechnology, the manipulation of matter on an atomic and molecular scale, has revolutionized various areas of science and everyday life [1] Some applications of nanoscience in everyday life include, electronic field,[2-6] medical field,[6-9]agricultural field [10,11], textile industry,[12,13] cosmetics [14,15]etc.

Electronics: Nano-sized transistors and circuits are used in electronic devices such as smartphones, computers, and televisions [2] Progress in nanoscale science has revolutionized the field of electronics, offering new possibilities for the development and advancement of technology.[3] These small components allow for faster processing speeds, increased storage capacity, and improved energy efficiency. For instance, nanomaterials have been utilized in the fabrication of smaller and more efficient electronic devices. Carbon nanotubes and graphene, have unique properties that allow for enhanced conductivity, flexibility, and durability [1] Additionally, nanotechnology has enabled the miniaturization of electronic components, leading to the development of smaller and more powerful devices, such as smartphones, tablets, and wearable devices. Furthermore, nanoscale fabrication techniques have allowed for the integration of multiple functionalities into a single device, resulting in the creation of multifunctional electronic systems that can perform tasks such as sensing, computing, and communication simultaneously[3]. These advancements in nanoscale electronics have also led to the development of more energy-efficient devices, as nanomaterials can enable better control over the flow of electrons, reducing power consumption and heat generation.

Medicine: Nanotechnology is used in medicine for drug delivery systems, targeted therapies, and diagnostic tools. For example, nanoparticles can be engineered to specifically target cancer cells, delivering medication directly to the tumor while minimizing side effects on healthy cells. They can be used to create imaging agents that can help doctors detect diseases at an earlier stage. These imaging agents can help differentiate between healthy and diseased tissue. Nanoparticles can be used to create scaffolds that can help regenerate damaged tissues. These scaffolds can provide a structure for new cells to grow on, promoting healing. They can be used to create implants that are more durable and biocompatible. This can lead to longer-lasting implants that are less likely to be rejected by the body. Nanoparticles based antibacterial treatments could help to combat the growing problem of antibiotic resistance. That means nanotechnology has the potential to revolutionize medicine by providing new tools for diagnosing, treating, and preventing diseases.

Materials: Nanomaterials are used in a wide range of everyday products, including sunscreen, stain-resistant clothing, and scratch-resistant coatings for eyeglasses and smartphone screens [14,15]. Many sporting goods, such as tennis rackets and bicycles, are made with nanomaterials that make them stronger and lighter. Nanoscale coatings can be applied to fabrics to make them water-resistant, stain-resistant, and wrinkle-resistant. Nanoscale zinc oxide and titanium dioxide are common ingredients in sunscreens. These particles can more effectively block ultraviolet (UV) rays without leaving a white cast on the skin. Nanoparticles can be used in stain removers to break down dirt and stains more effectively. They can be used in cosmetics to improve their delivery and effectiveness. For example, some moisturizers contain nanoparticles that can deliver hydration deep into the skin

Additional applications of nanoscience in everyday life include:- Energy: Nanotechnology is used in solar panels to improve their efficiency and reduce costs. Nanoscale materials and techniques are used to develop more efficient solar cells. Nanoparticles can increase the surface area of the cells, allowing them to capture more sunlight. They can also improve light trapping within the cell, leading to more efficient conversion of sunlight into electricity. Nanotechnology is being used to create better batteries with improved energy density, faster charging times, and longer lifespans. For instance, researchers are developing new electrode materials with higher capacities using nanomaterials. This is crucial for electric vehicles and storing renewable energy. They can be used as catalysts in fuel cells, which convert hydrogen fuel into electricity. These catalysts increase the efficiency of the reaction and can reduce the need for expensive materials like platinum. Nanotechnology can improve the efficiency of traditional energy sources like fossil fuels. For example, nanocoatings can be applied to drill bits used in oil and gas extraction, making them more durable and efficient. Nano sized materials are being investigated for storing hydrogen fuel more safely and efficiently. This is essential for developing a hydrogen-based economy. This technology holds immense potential for creating a more sustainable and efficient energy future. By improving existing technologies and developing entirely new ones, nanotechnology can help us address the global challenge of energy production and consumption.

Environmental: Nanotechnology is used in filtration systems and water treatment technologies to remove contaminants and improve water quality.[15-19] Pollution Remediation: Nanoparticles can be used to clean up pollutants in soil, water, and air. For instance, certain nanoparticles can absorb and break down contaminants like heavy metals and organic toxins. Nanofiltration membranes can be used to remove impurities from water, providing access to clean drinking water. Additionally, nano-catalysts can be used to degrade pollutants present in water sources. Nanomaterials can be used in air filters to capture pollutants more effectively, improving air quality. These filters can target harmful gases and tiny particles like allergens. Nanoscale sensors can be developed to detect environmental pollutants at very low concentrations. This allows for early detection of environmental issues and helps with targeted remediation efforts. Nanotechnology can be used to develop new materials that are more environmentally friendly. For example, nanocoatings can improve the durability and efficiency of solar panels or wind turbines. In essence, nanotechnology offers a multi-pronged approach to environmental issues. It can help clean up existing pollution, improve the efficiency of clean energy technologies, and develop new tools for monitoring and protecting our environment. However, it's important to remember that nanotechnology is a rapidly evolving field, and the potential environmental impacts of some nanomaterials are still being studied.

In conclusion, nanotechnology has become an integral part of our daily lives, revolutionizing numerous fields and enhancing the way we interact with technology, consume goods, and address healthcare needs. Its applications range from electronics to textiles, cosmetics to medicine, and even extend to food packaging and environmental remediation. Nanotechnology's ability to manipulate materials at the molecular level has unlocked a world of possibilities, allowing for innovations that improve performance, durability, and sustainability across diverse sectors. As we continue to harness the power of nanotechnology, its influence will undoubtedly continue to shape and enrich our everyday experiences, making our lives more efficient, convenient, and sustainable.

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Chapter 6

THE NANOTECHNOLOGICAL REVOLUTION IS MAKING ITS WAY TO THE NOBEL PRIZE IN 2023

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INRODUCTION

Nanotechnology deals with materials and structures of very low size ranges from 1 to 100 nanometres, which make it a cutting-edge area in science and technology. A nanometre is one billionth of a metre. On this nanometre scale, the unique properties of materials and their behaviour are revealed[1,2]. They can be manipulated and engineered by scientists and engineers for a variety of purposes. Nanotechnologies are having a major impact in all areas, e.g. electronics, pharmaceuticals, materials science and energy etc. And it has great potential for innovation and solving some of the world's biggest problems. New opportunities for developing innovative materials, devices and systems with unprecedented accuracy and efficiency have emerged in this area. The history of nanoparticles or nanotechnology dates back to 1959, when renowned physicist Richard Feynman first introduced the concept of Nano chemistry [3-5]. In this area, there have been certain developments and incredible growth. And the Nano technological revolution is making its way to the Nobel Prize in 2023.

In relation to this nanotechnology, certain terms are important and their correct interpretation also plays a role. 'Nanotechnology' is a study of nanoscales, and such understanding will be implemented and applied through 'Nanotechnology'. 'Nano chemistry' is a discipline that concerns the production, manipulation and application of materials with sizes ranging from 1 to 100 nanometres. ‘Nanomaterials’ are materials with a size in this range of 100 nanometres or materials that exhibit properties not found in the molecular and bulk solid state due to their size factor.

Electrostatic, Van der Waals, Brownian, Vibrational, Chemical and Quantum mechanical forces are the most powerful force of attraction for nanomaterials. There are two things that happen when a bulk material is transformed into a nanomaterial. The increase in surface area to volume ratio is the first. The surface area changes and volume is unchanged during the transition to a lower size[6]. Therefore, the surface area to volume ratio shall be increased and reactivity also increased. Quantum confinement is another thing that's happen during this transformation. It is the trapping of electrons and holes in tiny regions to restrict their motion which provides a method of tailoring or engineering the band gap of the materials. The quantum confinement effects lead to most fundamental manifestations of nanoscale phenomena in materials and frequently used for the study and development of nanoscience, particularly in semiconductor nanomaterials and quantum dots. As a result, nanomaterials have special chemical characteristics because of the high surface area to volume ratio and their extraordinary optical and electric properties based on quantum confinement.

HISTORY OF NANOTECHNOLOGY

The concept of nanotechnology was introduced by the famous physicist Richard Feynman at his lecture, ‘There's Plenty of Room on the bottom’. He explained in this discussion the possibility of chemical synthesis by manipulating atoms directly. In 1974, Norio Taniguchi came up with the term "Nanotechnology”. In 1986, inspired by Feynman's ideas, Eric Drexler, author of the book ‘Engines of Creation: The Coming Age of Nanotechnologies’, coined the term "Nanotechnology." it deals with the concept of a nanoscale assembler capable of creating copies of itself and other objects of arbitrary complexity with atomic precision. He also tried to promote a better understanding of the concepts and implications of nanotechnology among the general public. In the 1980s, his conceptual framework for nanotechnology, combined with high profile experimental developments, has increased public awareness of the potential for atomic control of matter, which has led to nanotechnology as a field of study. In the 1980s, the development of nanotechnology was greatly influenced by two major discoveries. First, a Scanning Tunnel Microscope(STM) was invented in 1981. It was successfully used for the manipulation of atomically different atoms from 1989 onwards. In 1986, the Nobel Prize in physics was awarded to the creators of STM, Gerd Binnig and Heinrich Rohrer. Binnig, Quate and Gerber had also developed an Atomic Force Microscope(AFM) that same year. Secondly, Harry Kroto, Richard Smalley and Robert Curl discovered the fullerenes in 1985. They've shared the Nobel Prize in chemistry in 1996. Nanotechnology was not first used to describe C60, instead, it was used to refer to later research on closely similar carbon nanotubes (also known as graphene tubes or Bucky tubes), which showed possible uses for nanoscale electronics and gadgets. Sumio Iijima was awarded the first Kavli Prize in Nanoscience in 2008 for his role in the discovery of carbon nanotubes[7].

This field attracted more scientific, political, and commercial interest during the last years. The Royal Society's study on nanotechnology is an example of the debates that have arisen around the definitions and potential effects of nanotechnologies. The public argument between Drexler and Smalley in 2001 and 2003 was the result of issues being raised about the viability of the applications that proponents of molecular nanotechnology had envisioned. While this was going on, the commercialization of goods based on developments in nanoscale technologies have emerged. These goods do not involve atomic manipulation of matter and are restricted to mass uses of nanomaterials. Examples include the silver Nano platform, which uses silver nanoparticles as an antibacterial agent, transparent sunscreens based on nanoparticles, silica nanoparticles used to reinforce carbon fibre, and carbon nanotubes used in stain-resistant textiles. Two examples of how governments have taken action to promote and fund nanotechnology research are the National Nanotechnology Initiative in the United States, which has a formal size based definition of nanotechnologies as well as funding for nanoscale research and the European Framework Programme on Research and Technology Development in Europe. In the middle of the 2000s, new and important scientific interests began to emerge.

RECENT ADVANCES IN NANOTECHNOLOGY

Nanotechnology is a rapidly evolving field with continuous advances and breakthroughs. It offers a wide range of benefits and has the potential to impact numerous aspects of our lives. Here are some notable areas of recent progress:

Nano medicine: Advances in targeted drug delivery systems using nanoparticles to improve the precision and effectiveness of cancer treatments. Development of nanoscale imaging agents for earlier and more accurate disease diagnosis.

Nano electronics: Continued efforts to push the limits of Moore's Law by developing nanoscale transistors and memory devices. For electronic components and interconnects, research on new materials such as 2D materials, e.g. graphene.

Quantum nanotechnology: advances in quantum computing and communications using nanoscopic bits. For applications in fields such as metrology and cryptography, development of quantum sensors and detectors.

Energy applications: Advancements in nanomaterials for more efficient solar cells, including perovskite solar cells. Research on nanomaterials for high-capacity and fast-charging batteries and super capacitors.

Nanotechnology in clean energy: research into nanomaterials to improve conversion and storage technologies, such as thermoelectric devices.

Environmental remediation: Use of nanomaterials, such as Nano catalysts, for efficient pollution control and wastewater treatment. Development of nanomaterial-based filtration systems for water purification.

Food and agriculture: Nanotechnologies in food packaging are used to extend shelf life and reduce food waste. Research into nanoscale delivery systems for precision agriculture, including targeted pesticide and nutrient delivery.

Nanorobotics: Progress in the development of nanoscale robots capable of performing tasks at the molecular level, including potential applications in medicine and manufacturing.

Nanotechnologies in space exploration: exploring the use of nanotechnology for spacecraft materials, propulsion systems and sensors that will be applied to future missions. Nano-ethics and safety: Growing attention to ethical considerations, safety protocols, and responsible research practices in nanotechnology[8].

Nanotechnologies have made major advances over the past years only in a couple of areas. With the potential to change various sectors and tackle global challenges, this area is developing at a rapid pace[9]. Nanotechnology provides us with the tools and knowledge to understand fundamental principles of science, making it possible for discoveries. While nanotechnology offers a number of benefits, it is necessary to take into account and address possible security, ethics or environmental concerns related to the field in order to achieve responsible development[10].

THE AMAZING GROWTH OF NANOTECHNOLOGY HAS REACHED THE NOBEL PRIZES

For the discovery and synthesis of quantum dots, Moungi G. Bawendi, Louis E. Brus & Aleksey Yekimov have been awarded a Nobel Prize in chemistry for 2023. Once the size of matter starts to be measured in millionths of a millimetre, strange phenomena start to occur – quantum effects – that challenge our intuition. Nobel Prize winners in chemistry of 2023 were all pioneer researchers into the world of nanotechnology. In the early 1980s, Louis Brus and Aleksey Yekimov were able to independently produce quantum dots, which are nanoparticles so small that they can be determined by quantum effects. In 1993, Moungi Bawendi revolutionized the production of quantum dots, making their quality extremely high, which is a prerequisite for their use in today's nanotechnology. With the laureates' work, we now have a chance to exploit some of the unique characteristics of nanotechnology. Quantum dots are now found in commercial products and used across many scientific disciplines, from physics and chemistry to medicine. These smallest components of nanotechnology now spread their light from televisions and LED lamps, and can also guide surgeons when they remove tumour tissue, among many other things.

The discovery of quantum dots was an important step in the development of nanoscience, and it inspired many chemists to engage in this interdisciplinary field. However, the modern field of nanoscience requires precise and ideally atom-level control of the synthesis of nanostructures. Therefore, the ability to fabricate materials at nanometre size and with sub-nanometre precision and high fidelity, safely, in benchtop chemical batch reactions represents a key milestone in the development of the field of nanoscience. This year’s Laureates played a central role in establishing these capabilities and in this way provided seeds for the rich field of nanoscience to grow.

DISADVANTAGES OF NANOTECHNOLOGY

Nanotechnology has many advantages, but it also brings its share of disadvantages and difficulties, such as:

Impact on the environment: Nanoparticles, due to their behaviour and toxicity may differ from bigger particles, can have an impact on the environment when released in ecosystems. The potential harm to marine and soil ecosystems is raising concerns.

Health concerns: The health effects of nanoparticles in inhalation, ingestion or absorption into the skin are currently being investigated. Some nanoparticles have been found to be associated with undesirable effects on health, raising concerns about worker safety and exposure for consumers.

Regulatory and ethical issues: In terms of setting safety standards and monitoring the release of nanomaterials into the environment, nanotechnology poses a challenge to regulatory authorities. Ethical issues are also brought to light, in particular as regards the use of nanotechnology for its intended purposes, which include improving people's lives and surveillance.

Costs and accessibility: Nanotechnology development and implementation can be costly, which may make it difficult to reach certain sectors or regions. It is a challenge to ensure equitable access to nanotechnology developments.

Risk of Nanoparticle Release: There is a potential for accidental release of nanoparticles into the environment, which may affect ecosystems and human health, while nanomaterial filled products are being produced, used or disposed of.

Nano ethics and governance: Ethical issues related to nanotechnology must be carefully considered and managed. It is still a matter of concern to establish ethical guidelines and frameworks for the management of research and development.

Public perception and awareness: Many people are not fully aware of the potential benefits and risks of nanotechnology. Effective communication and education efforts are needed in order to make informed decisions and take responsibility for the use of nanotechnology.

Security risks: The development of advanced nanomaterials and nanoscale devices may pose security risks if used inappropriately, such as in the development of new weapons or surveillance technologies.

Intellectual property issues: Innovation in research and development is often the basis of nanotechnology progress. Progress and access to critical technologies can be hindered by intellectual property issues.

CONCLUSION

Finally, nanotechnology has become a ground-breaking science discipline with huge implications for different areas. As we've explored, it has a rich history rooted in the manipulation of materials at the nanoscale, with significant contributions from visionaries like Richard Feynman and the coinage of the term "nanotechnology" by Norio Taniguchi in the 1970s. Nanotechnology covers a broad range of applications, from medicine to electronics, energy technology, materials science and the environment. Nanotechnologies are designed to deliberately control and manipulate matter in a range of 1 to 100 nanometres, creating unique properties and behaviours which can be exploited for the development of novel solutions.

It is remarkable that nanotechnology has progressed in such a way recently. Researchers have made progress in the field of Nano medicine, with a focus on targeted drug delivery and early disease detection, as well as promising more effective treatments and diagnostic tools. Nanotechnologies are pushing the limits of miniaturization and computing power, while quantum nanotechnology is a potential game changer in terms of computers and communications. In the area of energy applications, nanomaterials improving Solar Cells and Energy Storage Systems are making progress which will contribute to sustainable energy solutions.

Nanotechnology, with effective pollution control and clean water technologies, can be used for environmental remediation. In addition, nanocomposites are being developed with increased strength, lighter and more flexible properties as a result of material science advances. Nanorobotics, which promises molecular precision in fields such as medicine and manufacturing, is on the horizon. In order to ensure responsible development and use of nanotechnology, ethical considerations and safety protocols are increasingly being taken into account. In addition, the field has broadened to include space exploration where nanotechnology is being explored for various applications.

Finally, nanotechnology's history is marked by visionary thinkers, its scope is limitless, and its recent advances are shaping a future filled with innovative and transformative solutions to some of humanity's most pressing problems. Nanotechnology has the potential to transform industry, improve people's quality of life and tackle a wide range of world challenges as it evolves.

To fully understand the impact of nanotechnology on science, technology and society, it is necessary to keep a close eye on its ongoing research and development. How nanotechnology will affect society in the future is currently being debated by scientists. A wide range of new products, including consumer goods, Nano medicine, nanomaterials, electronics, biomaterial and energy generation can be developed by nanotechnology.

Nanotechnology, on the other hand, raises many of the same problems as any new technology, such as concerns about the toxicity and environmental impact of nanomaterials, as well as their ability to have an impact on the world's economy and the speculative possibility of numerous scenarios, such as the apocalypse. These concerns have led to discussions between activist groups and governments about the need for a specific nanotechnology regulation, which is currently under discussion. It is important to note that, while nanotechnology presents these disadvantages and concerns, the continued development of research, regulation and responsible practices with a view to addressing those challenges and maximising nanotechnologies' benefits as well as minimising their risks are constantly developing. Responsible nanotechnology development is underpinned by ethics and a thorough assessment of the possible consequences.

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Chapter 7

TITANIA NANO HYBRIDS- SELECTIVE APPLICATIONS

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Many challenges that have directly or indirectly impacted mankind in recent decades, such as environmental degradation, the energy crisis, metal depletion, etc., are now major research topics. Due to rapid industrialization, the demand for metals and alloys is growing in construction, aerospace, containers, packaging, transport, etc. [1]. At a time when environmental damage is a growing problem, corrosion is the primary cause of the depletion of our natural resources. It causes significant inconvenience to people and frequently results in fatalities [2]. Corrosion is the most important metal consumer known to man. It is one of the oldest problems that have ever challenged the industrial world and remains as a challenging problem in the 21st century. The durability and efficiency of metallic alloys can be improved by applying anti-corrosion coatings has been an active area of materials science for many years [3, 4]. Environmental pollution, especially water resources has increased in the last few decades including the agricultural, industrial, pharmaceutical and plastic industries[5]. The unmanageable discharge of several hazardous contaminants and pollutants into aquatic streams troubles human health. It comprises of 300–400 MT of filthy waste deposited annually by businesses, as well as sewage that is directly dumped into water bodies (World Water Assessment Programme United Nations).Water pollution raises environmental risks that can result in eutrophication, water scarcity, and even grave health risks for humans [6]. Adopting novel waste management techniques is a necessity in order to preserve the health of the global community and ecosystem. Research into the production of hybrid systems based on TiO_2 constitute a new group of compounds exhibiting strictly designed physicochemical properties have the potential applications in different fields[7]. This chapter presents a brief outline regarding its anticorrosion and waste water remediation applications.

Titanium dioxide is one of the most heavily investigated oxide materials in addressing energy and environmental crises. Among the different applications of TiO_2 hybrids, anticorrosion, adsorption, photocatalysis and wettability control over various fields as represented in figure 1.

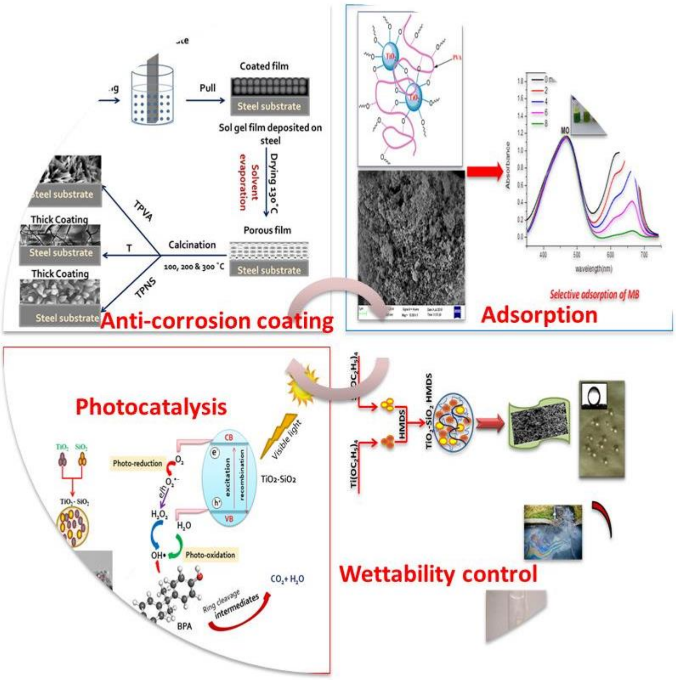
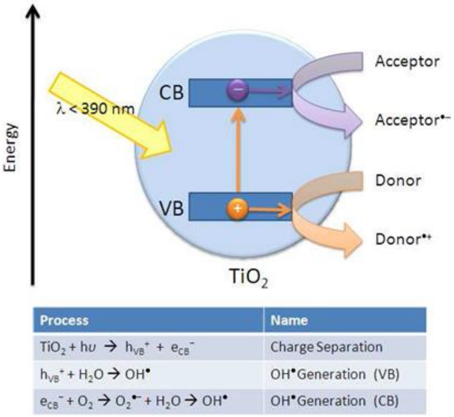


Figure 1.Image on the applications of TiO_2 hybrids.

Titania and titania based composite coatings on mild steel surface have always been a research focus for their versatile applications. They can be used as protective materials such as protective layers on metals surface to improve the wear and corrosion resistance. Guin et al. developed titania containing organic-inorganic hybrid sol-gel film using titanium isopropoxide as precursor and methyl hydrogen silicone as coupling agent. Nowadays hybrid metal oxide sol-gel coatings are widely accepted materials to improve corrosion resistance on various metals like Al, Mg, Fe and alloys. This is because they have good adhesion to metallic substrates and good barrier effect to corrosion substances. Hybrid sol-gel coatings have attracted attention of many researchers in recent years due to their ability to enhance the corrosion resistance of metal. The application of sol–gel coatings, infact has been projected as a better replacement for the environmentally unacceptable chromate conversion coatings. The titania hybrid sol-gel coatings over metallic substrates act as adhesion promoters and are used to protect the metals against corrosion. There are many advantages using sol–gel coatings. The most important features are listed as follows (i) sol-gel protective coatings have shown excellent chemical stability, oxidation control and enhanced corrosion resistance for metal substrates. (ii) sol-gel method is an environmentally friendly and cost-effective technique of surface protection. (iii) sol-gel coating showed the potential and are able to effectively replace environmentally unacceptable chromate conversion coatings (iv) sol-gel process has potential to be used for preparation of inorganic or organically modified protective coatings. (v) sol-gel procedure allows deposition of a thin oxide film even at room temperature. Sol–gel process is very attractive and versatile to prepare inorganic or hybrid films with tunable thickness. Moreover, mild synthetic conditions provided by sol–gel chemistry are advantageous for the incorporation of organic components into the inorganic network, allowing the preparation of a variety of hybrid architectures. Jaseela et al developed a stable, low cost thiourea doped titania- Poly vinyl alcohol (PVA) hybrid nano composite anticorrosion coating on mild steel via sol-gel dip-coating method. The coating on metal provides good protective efficiency, allowing the exposure period in 1M HCl to be extended to 70 days. This is significantly better than the traditional sol-gel coating, which gradually loses its effectiveness [8, 9].

A plethora of research has been done for the remediation of waste water. Water pollutant species present in water are micro-organism, pesticides, pathogens, and other organic materials. Dyes considered as type of organic pollutants and represent one of the problematic groups. They are emitted into water from various industrial branches exhibit toxic effects on microbial as well as mammalians. Most of the dyes used in textile industries are light-stable and not biologically degradable. A number of methods such as ozonation, coagulation, precipitation, ion exchange, have been used for the removal of dyes from water. Each of these methods has inherent limitation. These have been limited since they require high capital and operational costs. However, adsorption among them is considered as an effective and economical method. Adsorption is considered to be one of the best methods because of its effectiveness and low cost. Many traditional adsorbents, such as active carbon, zeolites, and polymeric materials, have been used for removing pollutants. TiO_2 is reported to possess a high adsorption capacity. But due to its poor mechanical stability might limit their practical application in some fields. The literature reports that modification into TiO_2 enhances the surface area by controlling the growth of crystallites and gives higher porosity leading to high adsorption efficiency. Apart from this the introduction of selective adsorbent is an important goal in the frontiers of research. The adsorbent can selectively adsorb one of the contaminant without any concentration change in the other molecules from a mixture. Factors that influence the adsorption efficiency include adsorbate-adsorbent interaction, adsorbent surface area, adsorbent to adsorbate ratio, adsorbent particle size, temperature, pH etc.[10] Numerous efforts have been taking on the construction of environmentally benign hybrids to enhance and extend the application to separate selectively dyes from contaminated water. Lim et al. synthesized sodium titanate nanobelts and nanotubes via hydrothermal synthesis using TiO_2 and TiS_2 as precursors respectively, and discovered that both nanostructures follow the Langmuir model in the adsorption of methylene blue (MB) [11]. The dual phase anatase/titanate nanoparticles reported by Cheng et al. also follow the Langmuir model in the adsorption of MB with a capacity of 162.19 mg g^{-1}. It was also reported that the removal of MB by anatase-covered titanate nanotubes follow the Langmuir model [12]. Jaseela et al proposed very simple, quick and practical method for the synthesis of inorganic –organic hybrid nanocomposite containing TiO_2 and PVA and investigated the remarkable adsorption selectivity for methylene blue (MB), from the mixture of methylene blue and methyl orange (MO) in aqueous environment. The nanocomposite exhibited 97.1% of MB removal within 8 minutes [13].

Photocatalysis is a promising, environmentally friendly technology for the conversion of solar energy into chemical energy. It is the acceleration of a chemical transformation by the presence of a catalyst with light. Common photocatalyst are semiconductors such as ZnO, TiO_2 Fe_2O_3 etc. When a semiconductor metal oxide is illuminated by light with energy equal to or greater than band-gap energy, the valence band electrons can be excited to the conduction band, leaving a positive hole in the valence band and an extra electron in the conduction band. Subsequent electron-hole recombination occurs when positive holes combine with promoted electrons to reverse the promotion process and releasing the input energy as heat, with no chemical effect. Nevertheless, if the electrons (and holes) migrate without recombination to the semiconductor surface, they may be involved in various oxidation and reduction reactions with adsorbed species such as water, oxygen and other organic or inorganic species other than the semiconductor itself. Photo-generated positive holes can react with electron donors to oxidise these molecules. Photo-generated electrons on the other hand tend to reduce electron donors exposed to the surface of the semiconductor. Three factors mainly pertaining to the band structure of semiconductor have the greatest effect on photocatalytic reactions. Generally, the photocatalytic power of a semiconductor widely depends: 1. Light absorption characteristics - Band gap energy determines which wavelength is more effective 2. Position of lowest point in the CB-determines the reducing power of catalyst and it should be negative with respect to the SHE potentials 3. Position of highest point in the VB determines the oxidizing power of catalyst and it should be positive with respect to the SHE potential**.** 4. Rate of redox reaction by electron-hole pair on the surface of semiconductor 5. Rate of e--h+ recombination has greatest effect on photocatalytic reactions. The wide band gap, high exciton binding energy, tunable crystal structure (rutile, anatase, and brookite), environmentally friendly nature of TiO_2 at nano scale have been employed to develop high capacity and selective sorbents for contaminants removal and in fuel synthesis namely in the field of Photocatalysis. Among the wide range of photocatalysts TiO_2 (Eg = 3.2 eV), WO_3 (Eg = 2.8 eV), $SrTiO_3$ (Eg= 3.2 eV), a-Fe_2O_3 (Eg = 3.1 eV), ZnO (Eg = 3.2 eV), and ZnS (Eg = 3.6 eV) in use, the most promising material is TiO_2, in view of its high photochemical activity. TiO_2 remains the most popular material and can be considered as a benchmark in the field of Photocatalysis. The report entitled "Autooxidation by TiO_2 as a photocatalyst" might be the first study regarding photocatalysis with respect to TiO_2 developed by Kato and Masho in the year 1956. In 1972, the main breakthrough towards TiO_2-based photocatalysis is reported by Honda and Fujishima by the discovery of water photolysis on a TiO_2 electrode. This was considered as the land mark study which aroused much attention and contribution towards photocatalysis. TiO_2 is really considered as a hot subject in the area of photocatalysis on account of the fact the number of publications exponentially growing till now. And it is interesting that studies have become more intensive in the last 20 years. In general, photocatalytic reaction on TiO_2 consists of three steps 1) photo-excitation generates electrons (e^-) and holes (h^+). 2) The electrons and holes migrate to the TiO_2 surface. Finally, the electrons and holes react with adsorbed electron acceptors and donors, respectively, to complete the photocatalytic reaction. The redox potential of photo-generated holes is + 2.53V compared with the standard hydrogen electrode (SHE). After reaction with water, these holes can produce hydroxyl radicals (OH.), whose redox potential is only slightly decreased. Both are more positive than that for ozone. The redox potential of conductive band electron is −0.52 V, capable of reducing dioxygen to superoxide $O_2^{\bullet-}$, or hydrogen peroxide H_2O_2.Depending upon the exact conditions, the holes, OH radicals, $O_2^{\bullet-}$, H_2O_2 and O_2, all can play important role in the photocatalytic reaction mechanisms. The mechanism of titania Photocatalysis is shown in the figure 2. Although the detailed mechanism of photocatalysis reactions of TiO_2 differs from one pollutant to another, it has been widely recognized that superoxide and, in particular, OH hydroxyl radicals act as active reagents for the degradation of organic compounds.



Process	Name
$TiO_2 + h\upsilon \rightarrow h_{VB}^{+} + e_{CB}^{-}$	Charge Separation
$h_{VB}^{+} + H_2O \rightarrow OH^{\bullet}$	$OH^{\bullet}$Generation (VB)
$e_{CB}^{-} + O_2 \rightarrow O_2^{\bullet -} + H_2O \rightarrow OH^{\bullet}$	$OH^{\bullet}$Generation (CB)

Figure 2. Mechanism of Titania photocatalysis

The extensive availability of visible light makes interest for the development of visible light active photo-catalysts. A small band gap is strongly desirable for an effective visible light photocatalyst. Much effort is currently focused on to meet these criterias and to harvest visible light (43% of the solar spectrum) for better solar energy conversion. A limitation of TiO_2 is its wide band gap of 3.2 eV which allows only UV light to be absorbed that covers limited area of solar spectrum (< 387 nm, accounting for 5% of the solar spectrum). So in order to achieve outstanding photocatalytic performance advances must be made to improve the light absorption, charge separation, and surface reactivity of TiO_2. Different strategies have been adopted to achieve the modification of the above-mentioned factors by either introducing morphological changes, such as increasing surface area and porosity, or by integrating additional components into the TiO_2 structure as chemical modifications. Figure 3 a) gives titania Photocatalysis under visible light and b) gives additional components influence. Important photocatalytic modifications can be obtained by surface modification of TiO_2. Modifications include: • the addition of transition metal ions (such as Cr, V, Zr, Mn, Fe, Mo); • preparation of the reduced form TiO_{2-x}; • sensitisation using dyes • doping with non-metals (such as N, S, C) • use of hybrid semiconductors such as TiO_2 /SiO_2 , TiO_2 /Al_2O_3 , etc. Fabrication of mesoporous titania hybrids as one of the most promising ways to achieve excellent photo-catalytic performance TiO_2. Recently, mesoporous and microporous oxides as well as their mixtures have become a rather popular research area. Zhou et.al.

determined the photocatalytic properties of a TiO_2 /ZrO_2 system obtained by the sol-gel method. Physicochemical analysis showed the material to have an anatase crystalline structure. The specific surface areas of the materials (for all variant methods of synthesis) lay in the range 187.0–219.2 m^2 /g.[14] Cheng et al. determined the photocatalytic properties of a hybrid material (UTZ) consisting of 3D nanospherical TiO_2 with a “hedgehog” shape and one-dimensional ZnO in the form of “nanospindles”. The resulting system was highly homogeneous and contained the crystalline structure of anatase (TiO_2) and the hexagonal wurtzite structure (ZnO) [15]. Yan et al. obtained a novel three-dimensional (3D) reduced graphene oxide/TiO_2 (rGO/TiO_2) hybrid composite by wrapping TiO_2 hollow microspheres with rGO sheets via a facile solvothermal route using poly(L-lysine) (PLL) and ethylene glycol (EG) as coupling agents.[16] Modifying the electron structure of titanium dioxide is the formation of hybrid oxide systems has been shown to have (i) modify the surface properties such as surface area of TiO_2 (ii) enhance thermal stability of the anatase phase (iii) enhance the electron–hole separation, (iv) extend the light absorption into the visible range Jaseela et al. used sol-gel hydrothermal process to create mesoporous titania (TiO_2) and titania-silica (TiO_2 - SiO_2) nanocomposites. The prepared Titania and its silica composites rapidly degrade an endocrine disrupting compound Bisphenol A (BPA) when exposed to visible light [17].

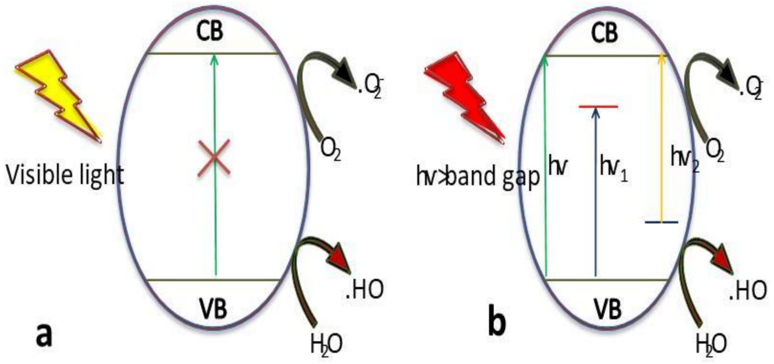


Figure 3 a) Titania Photocatalysis under visible light and b) effect of additional components on titania.

A solid surface that strongly repels water drops is called a superhydrophobic surface. Based on the contact angle and the wetting behavior, the solid surfaces are classified into four categories: (1) superhydrophilic, if the contact angle is less than 10, (2) hydrophilic, if the contact angle is between 10 and 90, (3) hydrophobic, if the contact angle is between 90 and 150, and (4) superhydrophilic, if the contact angle is above 150 . Contact angle is usually used as a measure of hydrophobicity or wettability. It is the angle made by the water drop with the contacting solid surface at the contact line. Understanding the wetting behavior of a water drop on a solid surface is the basis for designing a superhydrophobic surface. Numerous super-hydrophobic artificial surfaces have been created inspired by living creatures with unique wettability that possess super-hydrophobic properties. Nearly all methods for achieving superhydrophobicity consist of two steps: first, making a hierarchical surface roughness, and then surface modification of some materials such as fatty acids, fluoroalkyl silans, etc. by means of a low surface energy solution. Superhydrophobic surfaces and coatings have a unique behaviour against water droplets. This unique behaviour result into a new set of applications including self-cleaning, antibacterial, oil-water separation, corrosion resistance. To date, various strategies have been proposed for imparting superhydrophobic surface to substrates, such as template methods, colloidal self-assembly, sol–gel processing electro-spinning, layer-by-layer deposition, lithography and others.There have been many reports of oil contaminants in sea waters and rivers due to the leakage and sudden accidents. It has always been challenging and expensive to remove oil contaminants from water. Special wetting membranes with simultaneous superhydrophobicity and superoleophilicity making it a promising candidate for water purification. . Different methods have been introduced by scientists. Super hydrophobic cotton as filter material has been used recently.The development of bio-inspired special wettability in textile industries concerned with cloths/paper for oil (or organic solvents)-water separation. Many findings have also been reported for preparation of super-hydrophobic surfaces and the oil–water separation efficiency by using super-hydrophobic cotton fabric. Indranee et.al reported. Fluorinated silyl functionalized zirconia has been synthesized using the Sol-Gel process to create an extremely durable superhydrophobic coating on cotton fabrics. The integration of chemical stability, and photocatalytic activity of TiO_2 material enables the convenient removal of the contaminants by ultraviolet irradiation, and allows facile recovery of the separation ability, making it promising for sustainable and highly efficient oil-water separation applications [18].Li et al. reported a facile electrochemical anodizing method for fabricating porous TiO_2 membrane with special wettability. Fluorinated compounds are expensive, toxic, non- biodegradable can easily react with other materials and harmful to human health. Therefore, super-hydrophobic and super-oleophilic coated fabrics must be manufactured using fluorine and chlorine-free precursors. The wetting ability control on TiO_2 nanostructure, the rate of wetting property change, stability under UV, and mechanical strength should be carefully studied. The durability of the coating under severe environmental conditions is also an essential requirement for suitable application in oil–water separation. jaseela et al proposed a simple but feasible method to fabricate super-hydrophobic coating on cotton fabric via sol-gel process. , WCA reached up to 161.5°. In the work they focussed in the treatment of wastewater contaminated by oil which results from some industrial activities such as oil production, oil delivery, oil refining and petrochemical operation. Figure 4 showing water droplets on super hydrophobic titania hybrid coated a) fabric b) paper. The coated fabric can effectively separate a series of oil–water mixtures through an ordinary filtering process with high separation efficiency .The as synthesized fluorine and chlorine free coated fabric can be effectively utilized in various fields [19].

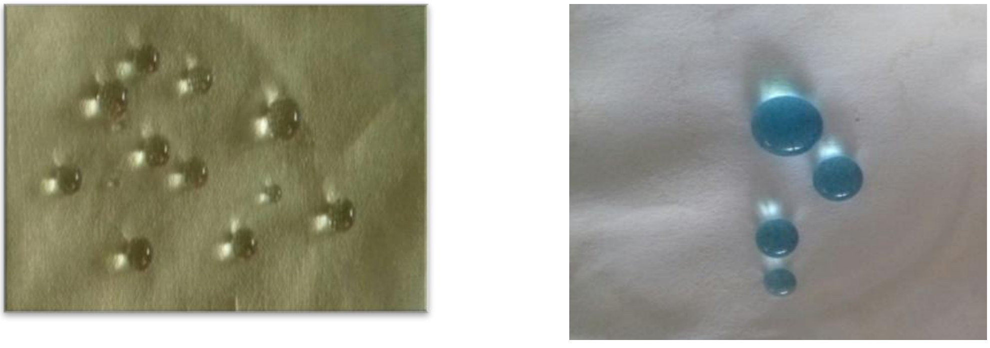


Figure 4. Water droplets on super hydrophobic titania hybrid coated a) fabric b) paper.

The degradation of the environment goes on increasing day by day by many ways. Among these metal degradation and water pollution are two major issues that have a direct impact on humanity and lead to huge problems. titania hybrids were found to have great potential in a variety of fields. This chapter presented a brief outline regarding its anticorrosion and waste water remediation applications. Apart from these, titania hybrids have broad potential for use in a variety of industries and fields, with extensive applications.

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Chapter 8

NANO-SIZED SOLUTIONS TO MICROPLASTIC POLLUTION

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Introduction:

Microplastic pollution, though small in size, looms large as a significant environmental threat. These tiny plastic particles, measuring less than 5mm, pervade our oceans, waterways, and terrestrial environments, posing grave risks to ecosystems, wildlife, and human health [1]. Despite their microscopic dimensions, the impact of microplastics is far-reaching, with concerns mounting over their persistence, bioaccumulation, and potential toxicity. Addressing this complex challenge requires innovative approaches, and nanotechnology emerges as a promising ally in the fight against microplastic pollution.

Nanotechnology, the science of manipulating matter at the nanoscale, offers unprecedented tools and techniques for studying, detecting, and mitigating microplastics. By harnessing the unique properties of nanomaterials, researchers can develop highly sensitive sensors capable of detecting even trace amounts of microplastics in diverse environmental samples. These nano-enabled sensors provide invaluable insights into the distribution, transport, and fate of microplastics, empowering scientists to better understand the scope of the problem.

Furthermore, nanotechnology facilitates the development of advanced filtration membranes and remediation technologies for removing microplastics from water sources. Nano-sized catalysts and photocatalysts offer efficient means of degrading microplastics, breaking them down into less harmful components. Additionally, nanomaterial-based tracers enable researchers to track the movement of microplastics in aquatic environments, shedding light on their ecological impacts [2].

In this chapter, we embark on a journey into the world of nanotechnology, exploring its role in addressing the challenges posed by microplastic pollution. Through innovative research and technological advancements, nanotechnology promises to revolutionize our approach to combating this pressing environmental issue, offering hope for a cleaner, healthier planet.

Nanomaterial-based Sensors

Nanomaterial-based sensors are advanced detection devices that utilize nanoscale materials to detect and quantify specific substances or particles, such as microplastics, with high sensitivity and selectivity. These sensors are designed to exploit the unique properties of nanomaterials, which can enhance signal transduction and improve detection limits compared to traditional sensing techniques[3].

One common approach in nanomaterial-based sensors for microplastic detection involves functionalizing nanomaterials, such as carbon nanotubes, graphene, metal nanoparticles, or quantum dots, with recognition elements that can selectively bind to microplastics. These recognition elements can include antibodies, aptamers, molecularly imprinted polymers (MIPs), or specific chemical receptors tailored to interact with microplastics.

When microplastic particles come into contact with the functionalized nanomaterials, they bind to the recognition elements, causing a change in the sensor's properties that can be measured and quantified. This change could manifest as alterations in electrical conductivity, optical properties, or electrochemical signals, depending on the sensing mechanism employed.

For example, in electrochemical sensors, nanomaterials are often used as electrode components due to their high surface area-to-volume ratio and excellent conductivity. When microplastics bind to the electrode surface, they can affect the electron transfer kinetics, leading to detectable changes in the electrochemical signal.

Similarly, in optical sensors, nanomaterials can enhance the sensitivity of detection by amplifying signals through mechanisms such as surface plasmon resonance or fluorescence quenching/enhancement. Functionalized nanoparticles can emit or absorb light in response to the presence of microplastics, allowing for rapid and sensitive detection.

Nanomaterial-based sensors offer several advantages for microplastic detection, including high sensitivity, selectivity, and the potential for miniaturization and integration into portable and field-deployable devices. These sensors play a crucial role in monitoring microplastic pollution in various environmental matrices, providing valuable data for environmental research and management efforts.

Surface-Enhanced Raman Spectroscopy

Surface-Enhanced Raman Spectroscopy (SERS) is a powerful analytical technique used for the detection and characterization of molecules, including microplastics, at extremely low concentrations. It combines the principles of Raman spectroscopy with the unique properties of nanostructured surfaces to greatly enhance the Raman scattering signals of molecules adsorbed onto or near the surface of certain materials.

In SERS, when a sample containing molecules interacts with a nanostructured surface, such as roughened metal surfaces or metal nanoparticles, it results in a dramatic enhancement of the Raman scattering signals [3]. This enhancement occurs due to two main mechanisms:

Surface Plasmon Resonance (SPR): When incident light interacts with metal nanoparticles or nanostructured surfaces, it can excite collective oscillations of conduction electrons called surface plasmons. This resonance phenomenon amplifies the electromagnetic field near the surface of the metal, enhancing the Raman scattering signals of nearby molecules.

Chemical Enhancement: The interaction between molecules and the surface of the nanostructured material can also lead to chemical enhancement mechanisms, where charge transfer processes between the molecule and the surface further enhance the Raman scattering signals.

The combination of these two enhancement mechanisms leads to significant amplification of Raman signals, enabling the detection of molecules at extremely low concentrations, even down to single molecule levels [4].

In the context of microplastic pollution, SERS can be employed to detect and characterize microplastic particles in environmental samples. Functionalized nanostructured surfaces or nanoparticles can be designed to specifically interact with microplastics, allowing for their selective detection amidst complex environmental matrices. By analysing the Raman spectra of the molecules adsorbed on or near the surface of the microplastics, researchers can identify the type, composition, and spatial distribution of microplastic particles with high sensitivity and specificity.

Fluorescence-based sensors

Fluorescence-based sensors utilize the phenomenon of fluorescence, where certain molecules absorb light at a specific wavelength and re-emit light at a longer wavelength, to detect and quantify target substances or particles, such as microplastics. In fluorescence-based sensors for microplastic detection, nanoparticles with intrinsic fluorescence or those functionalized with fluorescent probes are often employed.

Fluorescence-based sensors work in the context of detecting microplastics are like this:

Functionalization: Nanoparticles, such as quantum dots or fluorescent organic dyes, are functionalized with molecules that can selectively bind to microplastics. These molecules may include antibodies, aptamers, or specific chemical receptors that recognize and interact with the surface of microplastic particles

Binding: When the functionalized nanoparticles come into contact with microplastics in the sample, they bind to the surface of the microplastic particles through specific interactions between the recognition molecules and the microplastic material.

Signal Generation: Upon binding to the microplastic particles, the fluorescence properties of the nanoparticles may change. This change in fluorescence emission, such as an increase or decrease in fluorescence intensity or a shift in emission wavelength, serves as a signal indicating the presence of microplastics.

Detection: The fluorescence signal emitted by the nanoparticles is detected and quantified using fluorescence spectroscopy or imaging techniques. By measuring the intensity and characteristics of the fluorescence signal, researchers can determine the concentration of microplastics in the sample and obtain information about their distribution and properties [5].

Fluorescence-based sensors offer several advantages for microplastic detection, including high sensitivity, rapid response times, and the potential for real-time monitoring. Additionally, fluorescence spectroscopy allows for multiplexing, where multiple fluorescent labels can be used simultaneously to detect different types of microplastics or other contaminants in the same sample.

Conclusion

In conclusion, the applications of nanotechnology in the study of microplastic pollution present a promising frontier in environmental research and management.

Nanomaterial-based sensors, including Surface-Enhanced Raman Spectroscopy (SERS), Surface Plasmon Resonance (SPR), and fluorescence-based sensors, offer sensitive and selective detection methods for identifying microplastic particles in various environmental matrices. These advanced sensing techniques leverage the unique properties of nanomaterials to enhance detection sensitivity and provide valuable insights into the distribution, concentration, and properties of microplastics. By harnessing nanotechnology, researchers can develop innovative tools and methodologies to better understand the sources, transport pathways, and ecological impacts of microplastic pollution. Additionally, these nanotechnology-enabled approaches hold promise for informing pollution management strategies and mitigating the adverse effects of microplastics on ecosystems and human health. As we continue to advance our understanding and capabilities in nanotechnology, it is essential to explore interdisciplinary collaborations and sustainable solutions to address the complex challenges posed by microplastic pollution effectively. Through concerted efforts and continued innovation, nanotechnology offers a pathway towards a cleaner and healthier environment for current and future generations.

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Chapter 9

Nanocellulose Scaffolds in Tissue Engineering

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1. Introduction

Regenerative medicine is a broad field that incorporates research on self- healing wherethe body can uses its own systems. The idea of replacement of a damaged body part using biomaterials or materials from natural origin was proposed and applied over 4000 years ago. Recently by the technological advancements the living tissues were engineered, giving rise to the field of tissueengineering (TE). Thus, it is an important interdisciplinary science for regenerative medicine, which involves the development of tissues that reinstate, maintain and enhance the tissue functions. It is the fabrication of bio-artificial tissues *in vitro* and includes the *in vivo* alteration of cell growth and function through the implantation of suitable cells isolated from donor tissues and biocompatible scaffolds. Tissue engineering has already showed remarkable successes in producing avascular tissues and organs (e.g., skin, cartilage, bladder, etc.) and holds great promises for producing tissues and organs containing highlyorganized three-dimensional vascular structures. In the future, tissue engineeringis expected to result in more complex tissues and organs that will be useful in overcoming the need for organ donations, reducing the number of animals used in drug discovery and drug toxicity research, and facilitating the development of patient-specific smart diagnostics and personalized medicine. The nanomedicineapplications in tissue engineering can be used whichcreates a new horizon for the various future developments in the field of tissue engineering.

Tissue engineering involve combination of three main elements, namely cells, scaffolds, and biomechanical or biochemical signals (figure 1). Current research in the field focuses on the development of these three elements to answer basic questions and produce functional living tissue

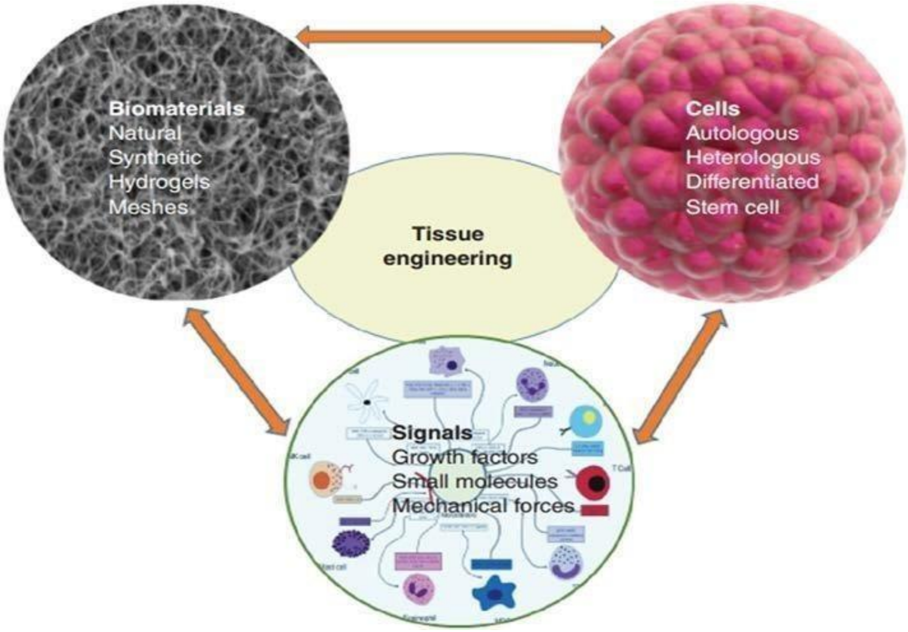

Figure 1. The triads of tissue engineering. Reproduced from ref. [1]

1. Structural and biological conditions for ideal scaffolds in tissue engineering

Scaffolds are polymeric materials that cause desirable cellular interactionsto form newfunctional tissues. The cells are seeded into scaffolds capable of supporting three-dimensionaltissue formation. They are used to support organs and organ systems that may have been damaged after injury or disease in tissue engineering. Scaffolds allow cell attachment and migration and retain cells and biochemical factors. They provide diffusion of vital nutrients and they can influence the behaviour of the cell phase mechanically and biologically.

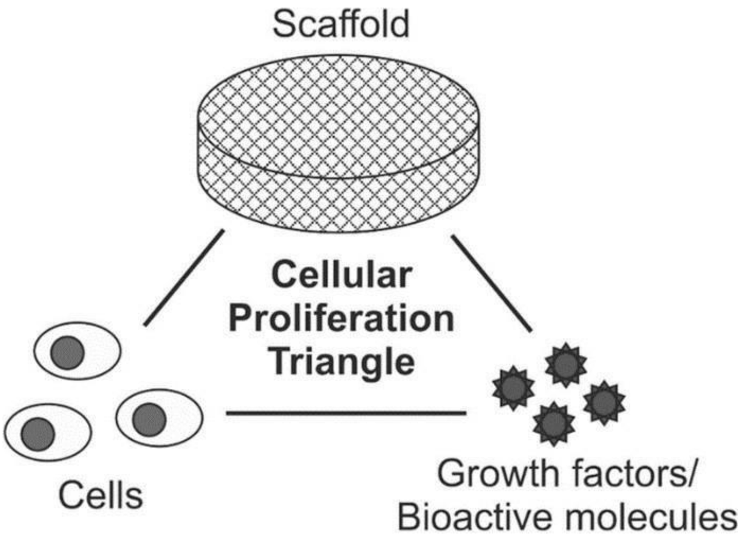

Figure 2. Cellular Proliferation. Reproduced from ref. [2]

Scaffolds prepared from the natural macromolecules has been used in tissue engineering rapidly. Scaffolds used can be directly implanted to promote the *in situ* cell growth, propagation, and regeneration of tissue without previous cell seeding. Scaffolds are of greaterimportance as they promote the tissue maturation and cell growth. Several researches have carried out in the development of usefulscaffolds in tissue engineering [3]. The basicconditions to consider a scaffold useful in tissue engineering are;

1. Biodegradability (easily degradable in normal pathways)
2. Biocompatibility (do not produce any toxic, response when exposed to bodyfluids)
3. Porosity (for the transportation of cell nutrients)
4. Similar mechanical performance
5. Structural morphology to a tissue of requirement in order to imitate the *invivo* nativetissue

2. Nanocellulose

Nanocellulose is cellulose in the form of nanostructures that possess the features not exceeding at least 1 dimension. These nanostructures comprises of the nanofibrils, found in bacterial cellulose; nanofibers, present particularly in the electrospun matrices and nanocrystals. The structures can be assembled further into bigger two-dimensional (2D) and three- dimensional (3D) nano, micro and macro-structures, such as nanoplatelets, membranes, films, microparticles, porous macroscopic matrices, etc. Nanocellulose can be obtained from bacteria,algae and plants. The crystallinity and the length to diameter ratio (L/d) are the parametersthatcontrol the properties of nanocellulose.

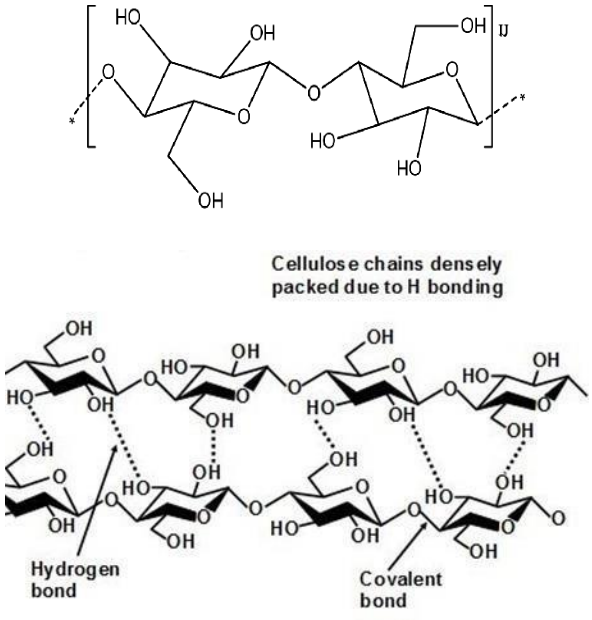

Figure 3. The structure of nanocellulose. Reproduced from ref. [4]

Scaffolds based on Nano-cellulose has direct application in the field of tissue engineering. Nano-cellulose based scaffolds are used due to their biocompatibility, water adsorption and retention and chemo-mechanical properties. The methods to prepare Nano- cellulose based scaffolds are electrospinning, 3D printing, solvent casting and freeze-drying. Nano-cellulose based scaffolds are raw materials for regeneration of different tissues and organsbecause of their distinct features. [5].

Since the β-1, 4-glucose in the molecular chain contains three active hydroxyl groups, NC can easily form hydrogen bond network, which has high mechanical strength and tailorablesurface modification. [6] The scaffolds based on nanocellulose are capable of engineering blood vessels, neural tissue, bone, cartilage, liver, adipose tissue, etc for repairing connective tissue and congenital heart defects. It can be also used for constructing contact lenses and protective barriers.

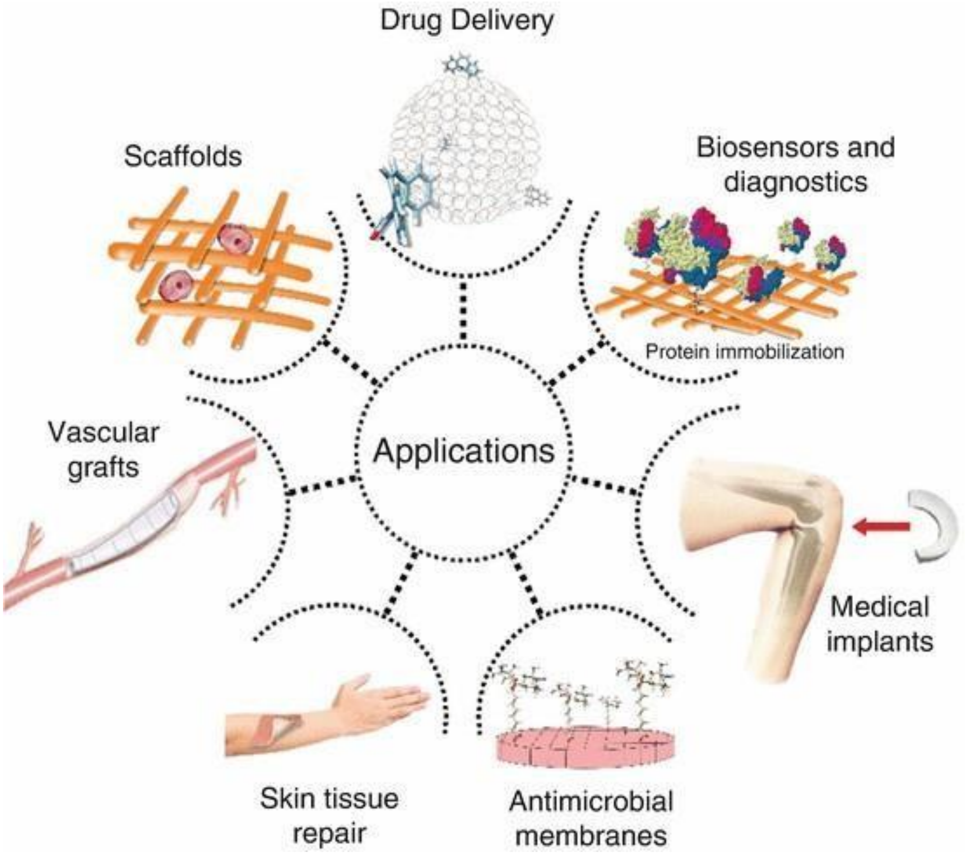

Figure 4. Applications of Nanocellulose Scaffolds. Reproduced from ref. [7]

3.1. Bacterial cellulose

Bacterial nanocellulose is produced by bacteria through the processes polymerization and crystallization. The glucose residues polymerize to β-1, 4 glucan linear chains in the bacterial cytoplasm and are secreted extracellularly. The developed chains are formed which are furthercrystallized to microfibrils. [8]. The microfibrils consolidate to highly pure 3D porous network of entangled nanoribbons of 20–60 nm in width. It is a hydrogel comprised of nanofibrils and imitates the fibrillary component of natural extracellular matrix. Certain mechanical properties of bacterial nanocellulose like elasticity, crystallinity, higher surface area, higher degree of polymerization, strength, Young's Modulus, conformability, water retention assists its use in skin reconstruction [9].

The bacterial nanocellulose is used profoundly in tissue regeneration due to its similarity and resemblance to the soft natural tissues. The advent use of bacterial cellulose as temporary skin substitutes for skin reconstruction was in 1990.The thin films of bacterial cellulose were used as substrates for the cultivation of human transformed skin keratinocyte in2006. From then bacterial nanocellulose are used in skin tissue engineering profoundly [10].

3.2. Plant-based nanocellulose

Plant nanocellulose are the cellulose materials isolated from the plant fibres. The versatile properties of plant nanocellulose paved its use in advanced applications. Cellulose nanofibers and cellulose nanocrystals are the two categories of plant nanocellulose. The cellulose nanocrystal has a rigid rod like structure that is 1–100 nm in diameter and its length is tens to hundreds of nanometer. [11] Whereas fibers possess length in micrometer range. They could be used as reinforcing agents for the development of nanocomposites with polymer matrices. Plant nanocellulose emerged as a promising material for skin tissue engineering. Reinforcing materials from plant-derived nanocellulose in theform of nanocrystals is used as degradable natural and synthetic polymers. [12] Cellulose nanocrystals (CNCs) synthesized by acid hydrolysis of cellulose fibresin HCl or H_2SO_4, have higher elasticity modulus, higher strength, larger surface areas, high crystallinity and bio-compatibilty. CNCs can be widely used to reinforce composites, collagen films and are the promising materials in skin tissue engineering [13].

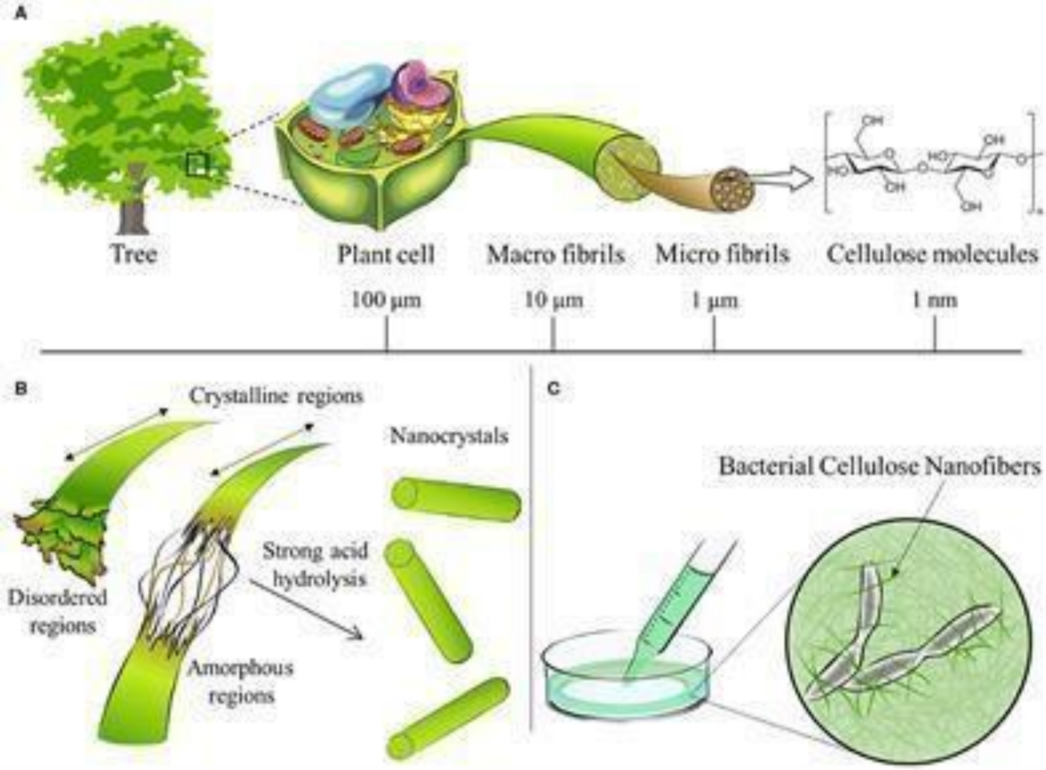

Figure 5. Types of nanocellulose: A) Plant nanocellulose, B) Nanocrystalline cellulose and C) Bacterial Nanocellulose. Reproduced from [14]

Properties of nanocellulose scaffolds

Nano cellulose has emerged as a promising material in the last 14 years. In2011 and 2012, there was a rapid increase in studies on the use of cellulose in technological applications such as bio-technology. In 2013, potential use of nanocellulose in tissue engineering, or the interaction of cells were studied [15]. In this study, composite membranes consisting of bacterial nanocellulose (BNC) and polypyrrole (PPy) were used as a template for seeding PC12rat neuronal cells. During the years from 2014, nanocellulose has been used in the interestingareas of tissue engineering like bone tissue engineering, liver tissue engineering, neural tissue engineering, cartilage tissue engineering, adipose tissue engineering ,vascular tissue engineering etc. [16]. The foremost paper with "nanocellulose" dedicated to the potential use of the

nanocellulose as a biomaterial for constructing tissue replacements was a study by Kramer in June 2006 [17]. The spark towards the work was inspired by effective properties of nanocellulose such as water absorption capacity, appropriate strength and elasticity, controllable shape, nanofibrous and porous structure, and biocompatibility. The main focus was on developing collagen-likematerials based on the composites of bacterial cellulose and synthetic polymers. The same group of authors published a second review in August 2006 which dealt with technical and biomedical applications of nanocellulose which includes creating artificial blood vessels, cuffs for nerve surgery, animal wound dressings, and cosmetictissues [17]. A very important paper on the use of nanocellulose in tissue engineering focusedon creating bacterial cellulose nanofibrous scaffolds [18]. These scaffolds were promising forvascular tissue engineering as they can promote adhesion of *in vitro* human vascular endothelial cells. The papers on biomedical application of nanocellulose with a review article by Klemm et al. discussed the types, sources, modes of preparation and properties of nanocellulose [18]. It dealt with bacterial cellulose and suggested that it can be a suitable material for organ implants, wound dressing, replacements of blood vessels and bone tissues. The future applications in the biomedical field by bacterial nanocellulose were reviewed in 2010 [19].

In vitro and *in vivo* studies suggest that nanocellulose scaffolds are non- toxic or minimally toxic. The implanted nanocellulose and injected nanocellulose are considered haemo-compatible and biocompatible. Biomaterial scaffolds should be biodegradable *in vivo* after the formation and regeneration of new tissue but nanocellulose scaffolds do not fully biodegrade [20]. Porosity is the crucial and important feature in the tissue engineering context.This arose the possibilityof tailoring porous 3D architectures while maintaining structural integrity and makes the use of nanocellulose effectively. The inter connectivity of the pores helps in the diffusion of cell nutrients and Though nanocellulose scaffolds have very high porosity, the mechanical strength of thenanocellulose is lower for its applications in stiffer tissues like cartilage and bone and load bearing locations and sites. The mechanical strength can be enhanced by the covalent cross- linking of nanocellulose maintaining highporosity. The cross linkers used can be tannic acid, 1, 2, 3, 4-butanetetracarboxylic acid (BTCA), sodium (meta) periodate. Structural morphologyof scaffolds play a crucial role for numerous factors like protein adsorption and cell adhesion which promote natural cellular functions. The scaffold anisotropy should be such that it should effect the cell growth significantly. Example, myoblast cells prefer to grow in the direction of nanocellulose alignment.

Cellulose nanofibrils were modified either by two ways profoundly. A negative electrical charge can be introduced by TEMPO-mediated oxidation or a positive charge introduced by 2, 3-epoxy propyl trimethyl ammonium chloride. It had been proven that the cellperformance on anionic-CNF (a-CNF) is better than cationic-NCF (c-CNF) [20].

1. Some limitations and methods to overcome

5.1. There are some limitations to the use of plant nanocellulose in skin tissue engineering,at times there is limited degradation of nanocellulose that can cause skin irritation and skin defects. The retention of non-degradable components cause scar formation. However, degradability can be induced by incorporation ofcellulase enzymes [21]. The introduction of N-acetyl glucosamine residues into the cellulose during the synthesis can yield degradable cellulose. These residues can be degraded in the human body by the wide spread enzyme, lysozyme [22]. The other method to yield degradable nanocellulose scaffolds is oxidation. The implantation of oxidized acetyl cellulose sponges in rats had degradation of about47% whereas ethyl cellulose had degradation of about 18% after 60 weeks. Regenerated cellulose, 2, 3-dialdehydecellulose (DAC) are degradable nanocellulose scaffold. **Skin tissue engineering**

Skin is the largest organ of the human body that stores water, fat, vitamin D. It has significant role in protection, sensation, immunization, and regulation. It is made up of two main layers epidermis and dermis. The hypodermis is present beneath the dermis. Skin tissue engineering is the reconstruction of the superficial skin layer epidermis, formed by keratinocytes and the skin inner layer dermis formed by fibroblasts.

The surface structured bacterial nanocellulose films provided an excellentplatform forthe growth, spreading and migration in keratinocytes by formation ofclusters. It formed a surface-structured 3D network of bacterial cellulose nanofibers. The biologically active molecules combined with bacterial nanocellulose accelerates the adhesion and growth of skincells. E.g., chitosan enriches the adhesion of the human keratinocytes on bacterial cellulose films [24].

Poly-pyrrole and polyaniline the electroactive composites of bacterial cellulose and conducting polymers are promising for skin tissue engineering.

Bacterial nanocellulose exhibitwound healing and speeds up infection prevention. Tuning the physical properties of bacterial nanocellulose with the combination of cellulose nanowhiskers with hydrogels helps in the drug release in the respective tissues. The silver nanoparticles along with the nanocellulose scaffoldsis used toavoid and reduce bacterial and microbial infections in the tissues [25].

The plant nanocellulose can be chemically modified by its conversion to cellulose acetate or to hydroxyethyl cellulose. It enhanced the electro spinnabilityof cellulose that supported the growth of mouse subcutaneous fibroblasts. Skin tissue engineering and wound dressing is highly benefitted by the blend of the cellulose acetate with gelatine. 3D Cellulose acetate scaffolds produced by spin-printing stimulated the metabolic activity of human

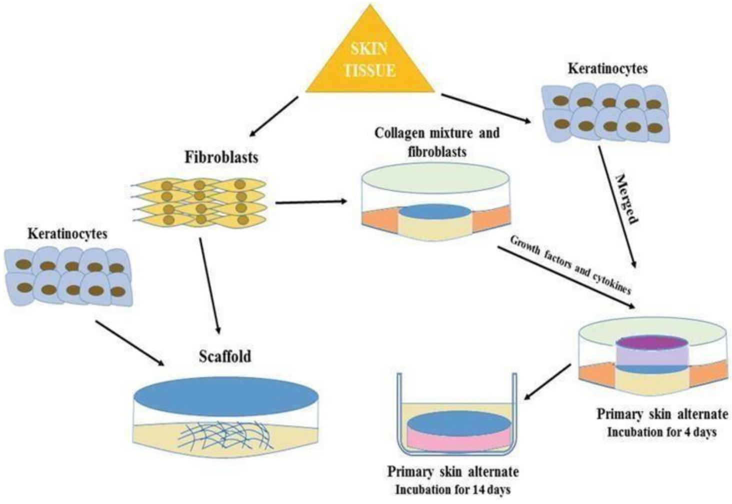

Figure 7. Depiction of the skin tissue engineering process by nanocellulose, [25].

5.1.Skeletal muscle tissue engineering

The skeletal muscles are those organs of the muscular system that are mostly attached by tendons to the bones of the skeleton system in the human body. The skeletal muscle consistsof uni-axially aligned muscle fibres assembled into fascicles. They propagate force on the bones by contraction in the same direction.The skeletal muscle cells are soft and fragile. The contractive forces are withstandby the connective tissue which furnish and assist the delicate muscle cells. Skeletal muscle play an important role in the physiological activities of blood vessels and nerves and their functionalities. Their coverings are routes of blood vessels and nerves.

An ideal tissue engineered skeletal muscle fibre should possess the contraction ability.Their functionalities and potentials should be similar to the native musclefiber. Electrospun cellulose nanocomposites and nanofibers (ECCNN) synthesized by electrospinning could be used for the skeletal tissue engineered fibre. When simulated human conditions are applied, the mechanical characteristics of the system can be compared to native tendons and ligaments.

These nanocomposites of engineered skeletal tissue possessed stable performance for cyclic loading and unloading [27]. Also, the irregular defects in the skeletal muscle can be rectified somewhat by the nanocellulose composites combined with gels. This can be used for the modification of the mechanical properties to clear the defects in the tissue engineered skeletalmuscle. The mechanically stable hydrogels can be prepared by cross-linking of hydrazide- functionalized POEGMA (poly (oligoethylene) glycol methacrylate) and aldehyde-functionalized NCC (A-NCC) and enhanced the dimensional stability.

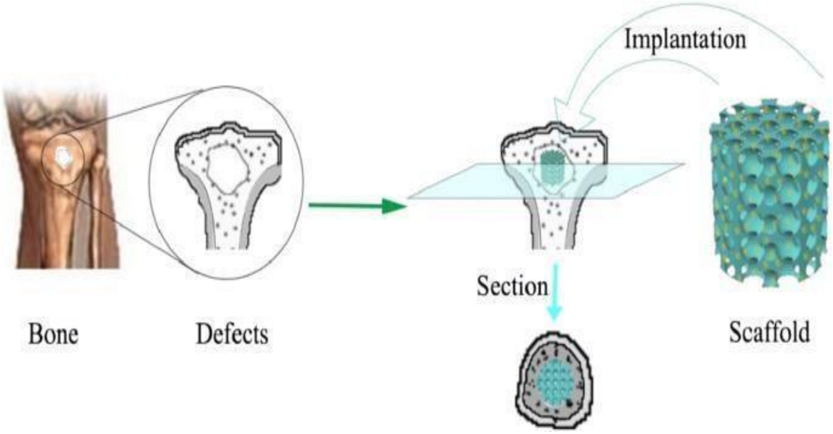

Figure 8. The representation of bone tissue engineering by nanocellulose scaffolds.

Reproduced from ref. [28].

Hydrogels can be used as bio-mimic scaffolds due to its remarkable properties of biocompatibility, controllable hydrogel anisotropy and tunable morphologies. The hydrogels used to make artificial muscle tissue by the monomer N-isopropylacrylamide and modified maleic anhydride NFC (MANFC) as the cross linker. The hydrogels formed were extensivelystretchable to more than 20 times theoriginal length. MANFC fibres are oriented largely to comprehend with the deformations which as a whole increases the tensile strength [29], https://www.sciencedirect.com/science/article/abs/pii/S0032386116304645].

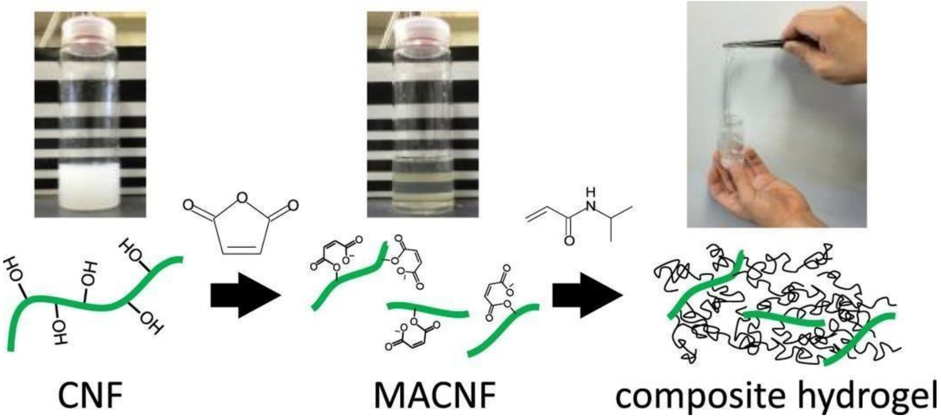

Figure 9. Surface modification of CNF with MA and the following hydrogel formation viainsitu polymerization of NIPAM. Reproduced fromref. [30].

5.2.Cardiac tissue engineering

Cardiac muscle tissue keeps the heart pumping through involuntary movements. The specialised cells that are pacemaker cells control the contractions of the heart. Cardiovascular tissue plays an important role in circulating blood for the transport of oxygen, carbon dioxide, nutrients, blood cells, and hormones and conserves the homeostasis of human body. Vascular grafts with nanostructured surfaces enhance the cell adhesion and proliferation. Cardio vascular diseases like heart valve disease, coronary artery disease, myocardial infarction, heart failure, pericardial disease, cardio myopathy. Simpledrug therapy is crucial and difficult to control theend- stage cardiac disease.

The composites prepared manifests promising applications in heart valves, cardiovascular substitutes and tissue engineered scaffolds. The 3D scaffolds for the tissue engineered cardiac should have the stability, flexibility and cyto- compatibility. The mechanicalstrength can be improved by crosslinking in NC based cardiac scaffolds. The potential toxicity of certain cross linkers can be avoided by single-component bioinks based on acetylated NFC (AceNFC) developed for direct ink writing which do not need cross-linking. The AceNFC bioinks required low concentration of nanofibrils and had favourable fidelity in dry and wet conditions. It possessed remarkable stability, biocompatibility with cardiac myoblast cells.

In another work a low-solid scaffold based on NFC, PLA were fabricated by 3D printing and manifested dryable and rehydratable properties deformation. NFC can accord to the printability and structural fidelity. Bio-inks should possess conductivity to restore normal conduction in damaged tissues for diseases such as arrhythmia. Conductive CNT patches wereprepared by 3D printed NFC/s ingle-walled CNT inks on BC. The patches formed are flexible, stretchable, and conductive in wet and dry conditions [31].

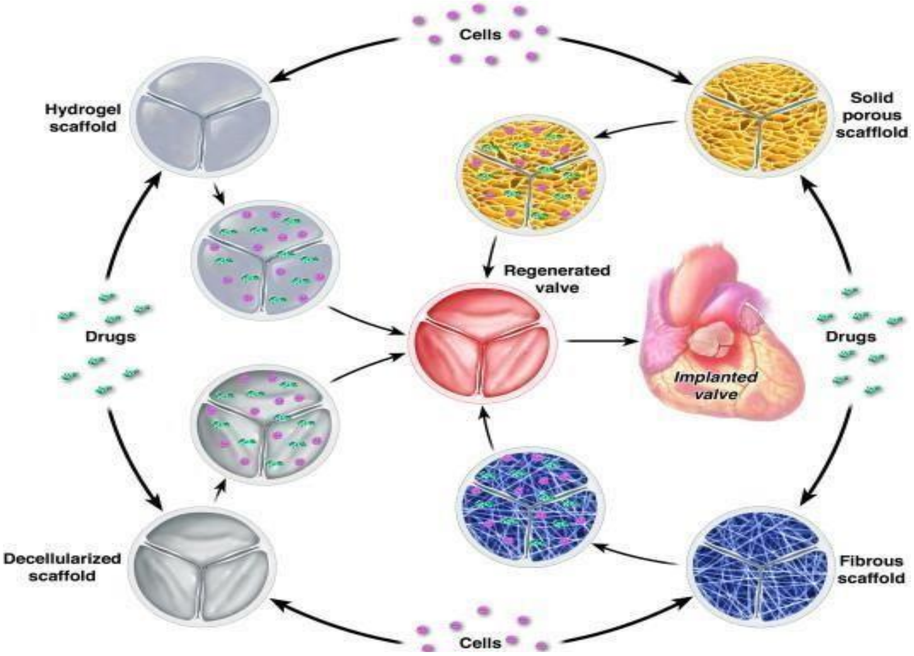

Figure 10. The cycle of processes in the cardiac tissue engineering [32]

5.3. Ophthalmic tissue engineering

The eye is a sensory organ that collects light, converts it into nerve impulses then the optic nerve transmits these signals to the brain and forms an image thereby providing sight. The human eyes comprises the two eyeballs surrounded by the orbit, the bony sockets of the skull. The eyes are protected by the fatty and fibrous tissue in the orbits. The eyelids, the conjunctiva, the lacrimal glands and the fibrous tunic (the outer coating layer of the eye).

Tissue engineered opthalmic tissue solve the problems by furnishing corneal regeneration implants, vision-corrective lenses and intraocular lenses. The requirement of ophthalmic tissue engineering is materials that possess excellent optical properties, efficient oxygen permeability, mechanical strength, better biocompatibility. Nanocellulose can be usedas an ideal material for the ophthalmic tissue engineering due to the properties like prominent water absorption, water

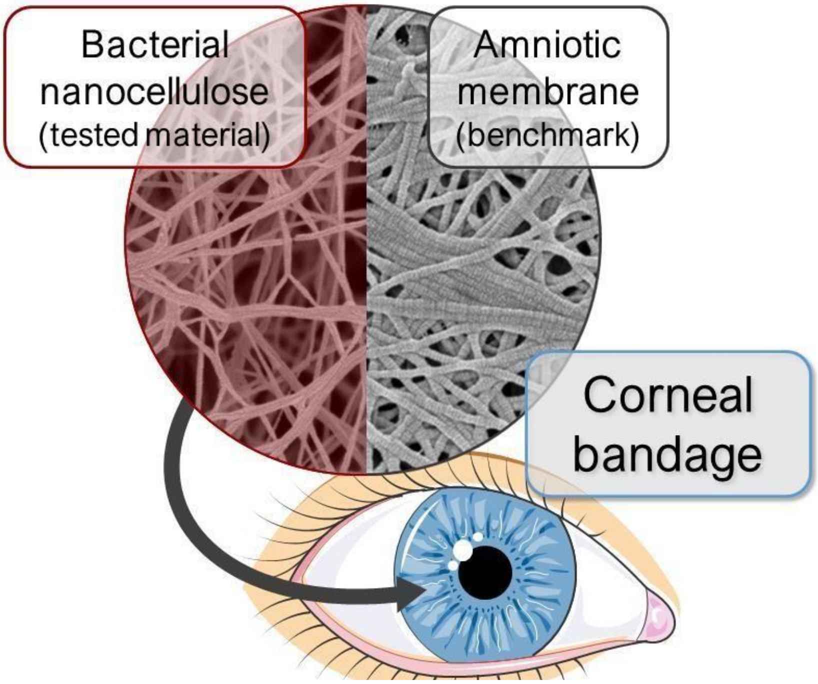

Figure 11. Bacterial nanocellulose corneal bandage. Reproduced from ref. [34].

retention, mechanical strength good compatibility and optical transparency due to the presence of large number of hydrogen bonds [33].

The hydrogel produced as such can promote and enhance the growth of human corneal epithelial cells. This acquires the potential for ophthalmic prostheses, disposable contact lenses, and corneal implants. For instance, the incorporation of PVA with NC can be used to produce a largely transparent macroporous hydrogel with more than 90 % water content. The visual acuity of ophthalmic devices can be improved by the NCC-PVA as it exhibited low light scattering when completely wetted. The excellent optical properties are shown by NCC or NFC in PVA hydrogel which are self-supporting hydrogels with large water content. The macroporous structures filled with water of hydrogel has a significant role in the provision of high oxygen permeability, low protein adsorption, and high wearing comfort. The viscoelastic and mechanical characteristics of hydrogels were influenced by the enhancement of NCC and solvent compositions.

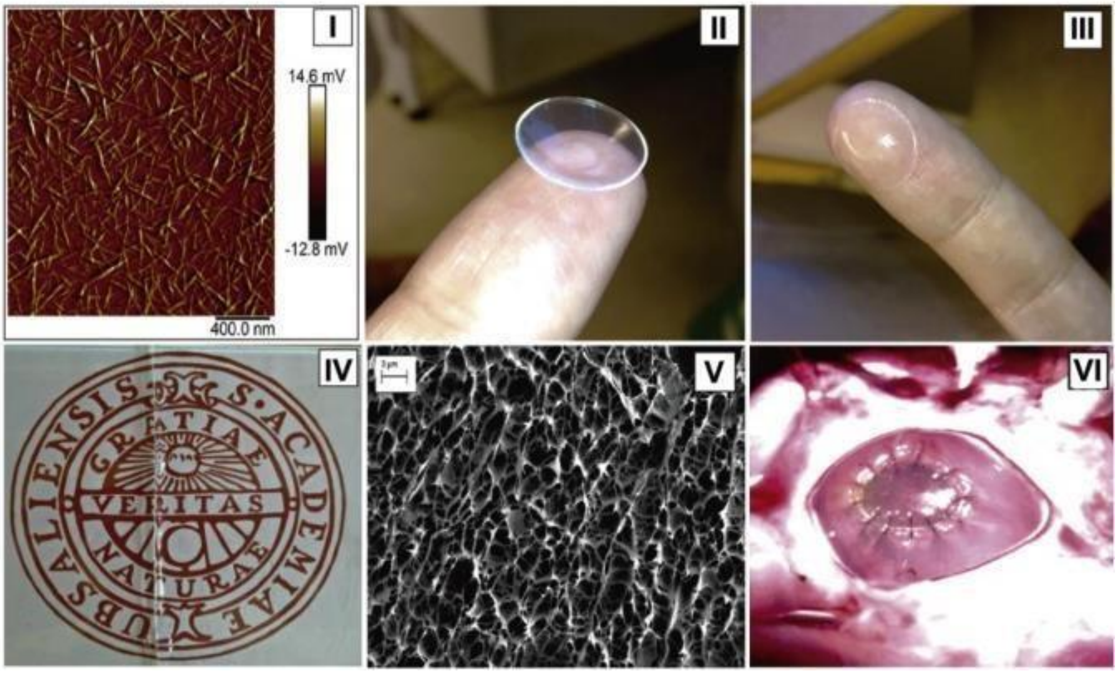

Figure 12. Tissue engineered eye lens. Reproduced from ref. [35]

5.1.Neural tissue engineering

The nervous system is the principal part of the human body that coordinates the behaviour and transmits signals between the body parts. The nervous systemis made up of a special type of cell called neurons at the cellular level. Neurons send signals in the form of electrochemical waves and travels through the thin fibres called axons. It releases the chemicalneurotransmitters at the junctions of other neurons called synapses. The nervous controls the internal environmental equilibrium and responds to the changes in the external environment. Itis dividedinto PNS which is the Peripheral nervous system and CNS which is the Central nervous system.

The rise of neural tissue engineering is due to the restricted capability of neural tissue to self- repair and regenerate after damage. The axonal development, the maintenance of the axon channel, the promotion of the neural stimulation and the activity can be carried out by theneural tissue engineered scaffolds. The cell behaviour can be induced correctly by the scaffoldswith eminent performances and these are of larger importance to the tissue engineered neural tissue.

Neural tissue engineered tissue can be made effectively from the electrospun NC- based scaffolds as they have controllable porosity, mechanical strength, orientation, and flexibility. 3D printing of neural tissue engineering scaffolds canbe done by conductive CNF or carbon nanotubes. It has an electrical conductivityof 3.8×10^{-1} S/cm to which the neural cells preferably attach firmly and propagate and differentiate [36].

The elastic modulus and tensile strength of the electrospun nanocellulose can be increased by the addition of 20% weight of NCC (based on nanocellulose). The direction of itsfibre orientation can be increased by almost 171.6 and 101.7% andenhances the thermal stability. The electrical conductivity of printed NFC/CNT (carbon nanotube) were 0.38 S/cm with the diameter less than 1 mm. They should incorporate to enhance and improve the development of neuronal cells and their nourishment. These developments are to be done in neuronal cells that tend to adhere, propagate and differentiate effectively. The *in situ* electricalstimulation and improvement in the fidelity of the 3D scaffolds improve the performance of the scaffolds used in the neural tissue engineering.

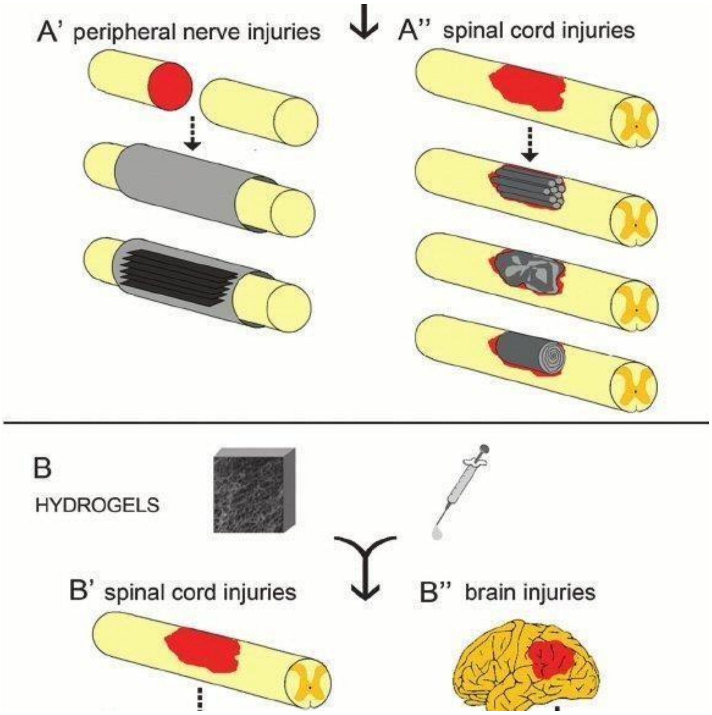

Figure 13. Treatment of nervous injuries by hydrogels. Reproduced from ref [37].

1. Future Prospects and Challenges of Nanocellulose Scaffolds in Tissue Engineering

The establishment of nanocellulose based scaffolds for tissue engineeringhas undergone a significant and substantial progress. The simpler scaffold formation methods andtheir mechanical features created numerous possibilities for the future prospects and applications of nanocellulose. The major challenges that occurred in the formation of scaffoldsis the combination of high porosity and apt mechanical performance. There is a gap between the research of nanocellulose scaffolds and their use in the commercial field. Therefore *in vivo* and *in vitro* studies should be done to bridge this gap. There is clinical demand, which enhance the development of tissue engineering technology for the treatment of the sorelydamaged tissues or organs. NC based scaffolds meet the requirements of an

effective tissue engineered though it has superior water absorption, water retention, biocompatibility, and mechanical properties.

The synthesis of nanocellulose scaffolds by additive manufacturing and biofabricationis effective for the emergent tissue engineering techniques. The different shape and size of thematerials can be customized by 3D printing and it is highly useful in the biomedical purposes. 3D printed materials can be used in the bone regeneration like collagen-based scaffolds loadedwith bone marrow stem cells set out as *ex-situ* miRNA delivery systems. But a major challengearises in this is there is shrinkage or swelling in the resultant materials after 3D printing.

In skin tissue engineering, the direct use of nanocellulose is not much advantageous due to its non- degradability in human organism. The scaffolds thatpersists in the skin lead to scar formation and complications. Therefore, nanocellulose can be used as a temporary carrierfor the delivery of cells into the wounds and it can be eliminated when the cells have adhered to the wounded region. But, the *in vitro* construction of artificial skin used for the experimental purposes such as for metabolism, vascularization of skin tissue, effects of drugs on tissues of various organs in the body and various studies in biology. Nanocellulose can be used as a material for the fabrication of epidermal electronics. It can be used as an advanced dressing material for systematic utilization of various drugs, transparent dressing material to allow, permit the direct inspection of wounds.

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[40] Three dimensional printed polycaprolactone microcrystalline cellulose

Chapter 10

Role of Ruthenium Nano-complexes in Chemotherapy

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According to the world health organization (WHO), cancer is a group of diseases characterized by uncontrolled growth of abnormal cells which can invade and spread to distant organs or tissues of the body. This perhaps leads to fatal consequences and remains as one of the significant causes of mortality worldwide. There are various types of treatments for cancer, but none of them is sufficient to eradicate the disease. Every year, a considerable amount of money is being invested for cancer research and each year, a new drug candidate is introduced to the pharmaceutical industry. However, these initiations have not made any considerable change in the increasing number of cancer patients and the disease remains a serious threat to humanity.

After the success of cisplatin, nearly 40 platinum-based agents were investigated clinically as anticancer drugs. Commonly platinum-based drugs inhibit DNA synthesis through covalent binding of DNA molecules to form intrastrand and interstrand DNA cross-links. Carboplatin, oxaliplatin, nedaplatin and satraplatin are the successful anticancer agents from the platinum family (Figure 1). Oxaliplatin followed a different mechanism than that of cisplatin because of its bulky nature. Satraplatin is an octahedral platinum(IV) complex, the most promising antineoplastic agent who can provide orally for the treatment of advanced prostate cancer which is now under clinical trials. All platinum-based drugs face same issues such as dose-limiting side effects and inherent or acquired resistance for cancer mainly because all of them followed the same mechanism without any up-gradation. Low selectivity of platinum drugs leads to off-target side effects like nephrotoxicity, myelosuppression, neurotoxicity, neuropathy, thrombocytopenia, neutropenia, ototoxicity etc. However, more efficient, less toxic, target-specific and non-covalently DNA binding non-platinum anticancer metallodrugs are in crucial need to treat cancer effectively.

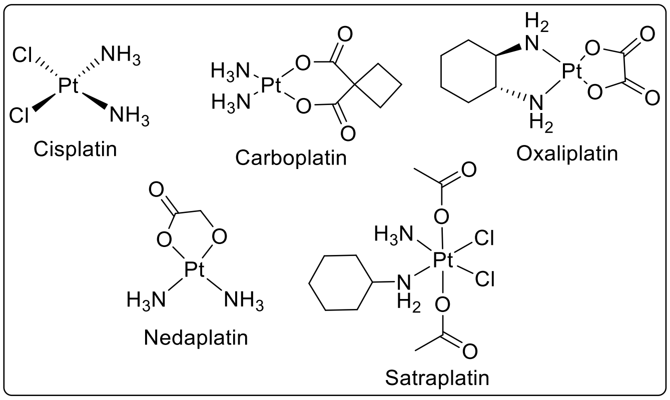

Figure 1. Platinum-based anticancer agents

To design the broad spectrum of metallodrugs for anticancer treatment, synthesize of complexes that can interact specifically to cancerous cells and lead to apoptosis without causing serious damage to normal tissues is required. Amid transition metal complexes, ruthenium complexes are established candidates in the search for new diagnostic and therapeutic agents. Less toxicity, easy absorption, effective bio-distribution and excretion are the main reasons for growing interest for ruthenium metallodrugs.

Ruthenium belongs to group 8 transition metals and almost inert to most of the chemicals and Russian chemist Karl Karlovich Klaus discovered it in 1844 from platinum residue. This can quickly form complexes with organic compounds and displayed excellent electronic and energy transfer properties. Structural and functional diversity of the complexes grasp massive attraction towards ruthenium chemistry and make it a star metal. All leading publications in science stream highlight the advancements in ruthenium complexes and their application in biology, medicine, catalysis, nanoscience, redox and photoactive materials etc.

Following factors are considered as the primary reasons behind the fast growth of ruthenium family of complexes in medicinal field.

i. Soft nature with moderate reactivity which favours coordinating N and S atom containing organic moieties.

ii. Reliable methods are available for synthesizing stable ruthenium complexes with predictable structure.

iii. Range of oxidation states exhibits from -2 to +8 among which Ru^{+2} and Ru^{+3} form stable complexes.

iv. Rate of ligand exchange is in the range of 10^{-2} and 10^{-3} S^{-1} under physiological pH that can be tuned by varying ancillary ligands.

v. For platinum metal, only four coordination sites are available to engage the ligands, whereas ruthenium has two other axial positions (Octahedral geometry) to interpret the steric and electronic properties.

vi. Ruthenium is a congener of iron, so it can mimic the binding nature of iron with a variety of biomolecules like human serum transferring. This makes ruthenium metallodrugs less toxic with minimal side effects compared to platinum drugs.

vii. Activation by reduction mechanism has been followed by some ruthenium agents who demonstrate more target specific actions.

Ruthenium complexes can interact with intracellular and extracellular targets in the human body and their interactions causes' cell damage. Another peculiarity of ruthenium is that it can organise certain organic drugs in definite shape and make it accessible for interaction. In both ways, ruthenium can increase its selectivity which is lacking in conventional drugs. In addition to this, luminescent ruthenium complexes can be used as sensors for cancer identification. Different families of ruthenium have been developed and checked their cytotoxicity against various carcinomas.

Only three ruthenium complexes namely NAMI-A, KP1019 and NKP1339 are entered into clinical trials till now (Figure 2). They are structurally similar but followed different mechanism of action. NAMI-A has failed to become a drug during Phase-II trials because its molecular level mechanism could not explain completely. This leads to further scope for conducting more researches in this field. Ruthenium complexes, in general, have a preference over DNA binding that create conformational changes in DNA double helix and obstruct the process of transcription which directs to cell death following other responses.

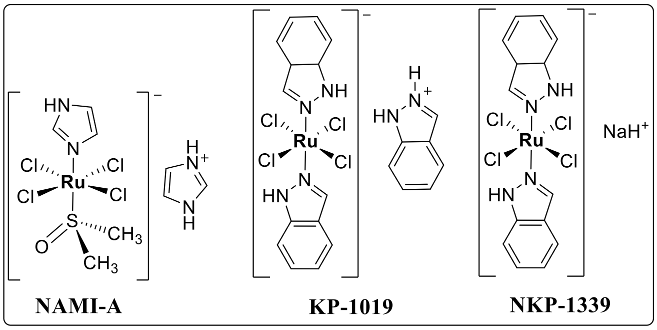

Figure 2. Structure of selected ruthenium complexes under clinical trial

Organic moieties in biological fluids are coordinated with various metal ions, especially transition metals, and showed superior activity compared to their free form. Almost all transition metal complexes have been analysed for their biological applications, especially complexes with organic derivatives of hydrazone as a ligand. Among transition metals copper(II), ruthenium(II), iron(III), cobalt(III), nickel(II) and zinc(II) established better application at the cellular level. Ruthenium complexes exhibit interesting biological activities in the presence of biologically reliable ligands. Schiff base compounds are an excellent option for ligand because they are capable of forming a coordinate bond with azomethane and phenolic groups. Ruthenium complexes can interact with intracellular and extracellular targets in the human body and their interactions causes' cell damage. Another peculiarity of ruthenium is that it can organise certain organic drugs in definite shape and make it accessible for interaction. In both ways, ruthenium can increase its selectivity which is lacking in conventional drugs. In addition to this, luminescent ruthenium complexes can be used as sensors for cancer identification. Different families of ruthenium have been developed and checked their cytotoxicity against various carcinomas. Among them ruthenium arene system is more promising and less explored. Arene played an imperative role in stabilizing the oxidation state of the Ru(II) metal centre contributing three pair of electrons and adopt three-legged piano-stool structure. Changes in the substitution, size or hapticity in the arene moiety can drastically affect the thermodynamic and kinetic parameters of the complex. Arene ligands help diffusion through cell membrane which enhances the cellular uptake of the drug. The halogen group can easily hydrolyse under the physiological condition which leads to the enhancement of drug activity. Bidentate chelating ligand contains NN, NO, OO or SO coordinating atoms that can influence redox potential of the central metal and nucleobase selectivity.

Organometallic complexes found active when organic-based prodrugs are no more effective towards certain cancer development. Organic compounds can bind with hydrophobic parts of the proteins but their activities are observed to be enhanced when it is coordinated with a specific transition metal, especially ruthenium metal and the obtained complexes showed predominant activity against inhibition of a range of cancer growth. Selective drug action for the specific type of cancers can be achieved by structure-based drug design. Choosing an apt precursor complex is vital, similarly, the ancillary ligands and the organic ligand moieties also needed to select as per the requirement.

Half-sandwich d^6 ruthenium complex [Ru(benzene)Cl_2(metronidazole)] was initially synthesized by Tocher *et al.*, in which the ligand is an organic anticancer drug. Studies revealed that cytotoxic activity of the ligand gets enhanced after complexation. This initiated a new challenge in the half-sandwich ruthenium chemistry where the complexes are renowned for their stability and reactivity. These arene ruthenium complexes present piano-stool geometry, where arene forms the seat of the piano-stool and remaining coordinating ligands take the place of legs. Three coordination sites of ruthenium are satisfied by arene part and remaining three sites are satisfied by other chelating ligands. The arene part helps to stabilize the complex and also provides lipophilic phase in order to interact with cell membrane. Drug design can be done by modification in arene ligand, its functionalisations and by introducing different types of monodentate, bidentate or tridentate ligands. Depending on the nature of the ligand moiety, the complex may become neutral or charged. These features can aid in tuning the pharmaceutical properties of the complex such as cell uptake and possible interaction with biomolecules. If there is a halide group in the coordination, it helps to replace it with water molecule and becomes a more reactive species.

Pseudo-octahedral piano-stool structured ruthenium arene complexes have been reported by M. Palaniandavar *et al*., where arene moiety is either benzene or p-cymene and ligands like diazacycloalkane derivatives. They showed prominent cytotoxic activity against the growth of MCF-7 breast cancer cell lines. Cationic nature of the complexes that helped to pass through the cell membrane is one of the reasons behind its anticancer nature. Annie Castonguay *et al*., came up with an innovative idea by considering catalytic metallodrugs as a solution for negative aspects of chemotherapy. Dose dependent less toxic but highly effective cancer drugs can be developed by making structural changes in schiff bases. To prove this, anticancer activity and catalytic potential of a group of ruthenium(II) arene complexes were carried out. Cyclohexane and furan substituted bidentate N, O donor schiff base ligands were used for the synthesis of one set of complexes that obtained readily by mixing with $[Ru(benzene)Cl_2]_2$. Reduction of these two ligands with $NaBH_4$ in methanol provided amine analogue of the schiff base ligands which allowed reacting with ruthenium arene precursor produced a sets of products along with an unexpected set. *In vitro* antiproliferative activity of the complexes checked against A2780, SH-SY5Y, MCF-7 and T47D cell lines. S. De *et al*., synthesized and analysed the anticancer properties of ruthenium arene system as shown in the figure 3. They designed the complex in such a way that maximum efficacy will be the outcome and they obtained the expected result.

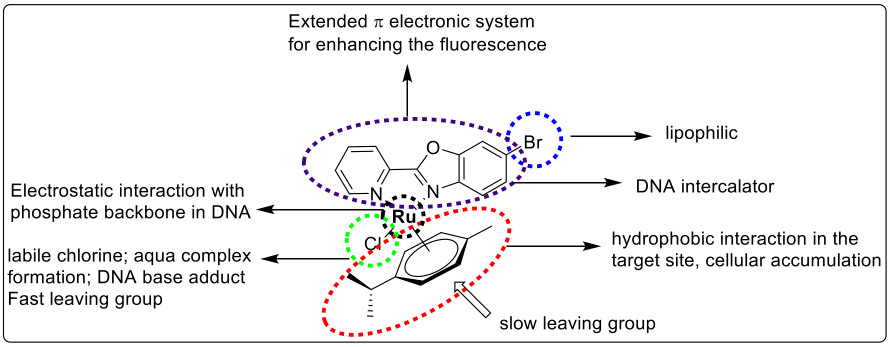

Figure 3. Structure activity relation of Ru-BOZ complex

In a recent article Sodio C. N. Hsu *et al*., successfully prepared three new Ru(II)-*p*-cymene complexes, from pyrazole based ligands and taken [$RuCl_2$-(η^6-*p*-cymene)] as dimer. All the synthesized complexes are well characterised using a range of spectral techniques. Binding affinity towards DNA was found through viscosity measurement, spectroscopic and docking studies. They also proposed the aqua form of the complexes in physiological conditions and their binding activities towards topoisomerase-I through *in silico* studies. *In vitro* cytotoxicity analysis of the complexes against triple negative breast cancer cell lines (TNBC MDA-MB-231) were also done and found that complex which has bidentate ligand shows good activity, this is compared to other reported similar complexes and therefore proved its superior anticancer activity.

Our research group have designed and synthesized organoruthenium complexes paired with *p*-cymene as the lipophilic part, N, O atoms of hydrazone ligands and chlorine as the leg. Further, investigated the activities of these synthesized complexes by theoretical calculations as well as experimental results. The pyrazole moiety was incorporated in the complex design wisely to make the complexes more potent towards cancer cells. The heterocyclic moiety will help to maintain strong interaction with biomolecules. The structures have been resolved with the help of single-crystal XRD studies. DNA binding and bovine serum albumin binding studies have been done using UV-visible spectroscopy and fluorescence spectroscopy. From these results, the intercalating nature of the complexes is identified and confirmed by *in silico* studies. Anticancer activities on cancer cell lines have been studied *in vitro*. LDH and NO assays were done and the outcome is found promising.

Thus Ruthenium based nano complexes can be considered as the future drug candidate for cancer therapy with less or nil side effects. Studies are ongoing to find the exact mechanism of action of such Ruthenium based drugs. Once the scientists could crack the puzzle, that will be the ultimate solution for cancer.

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