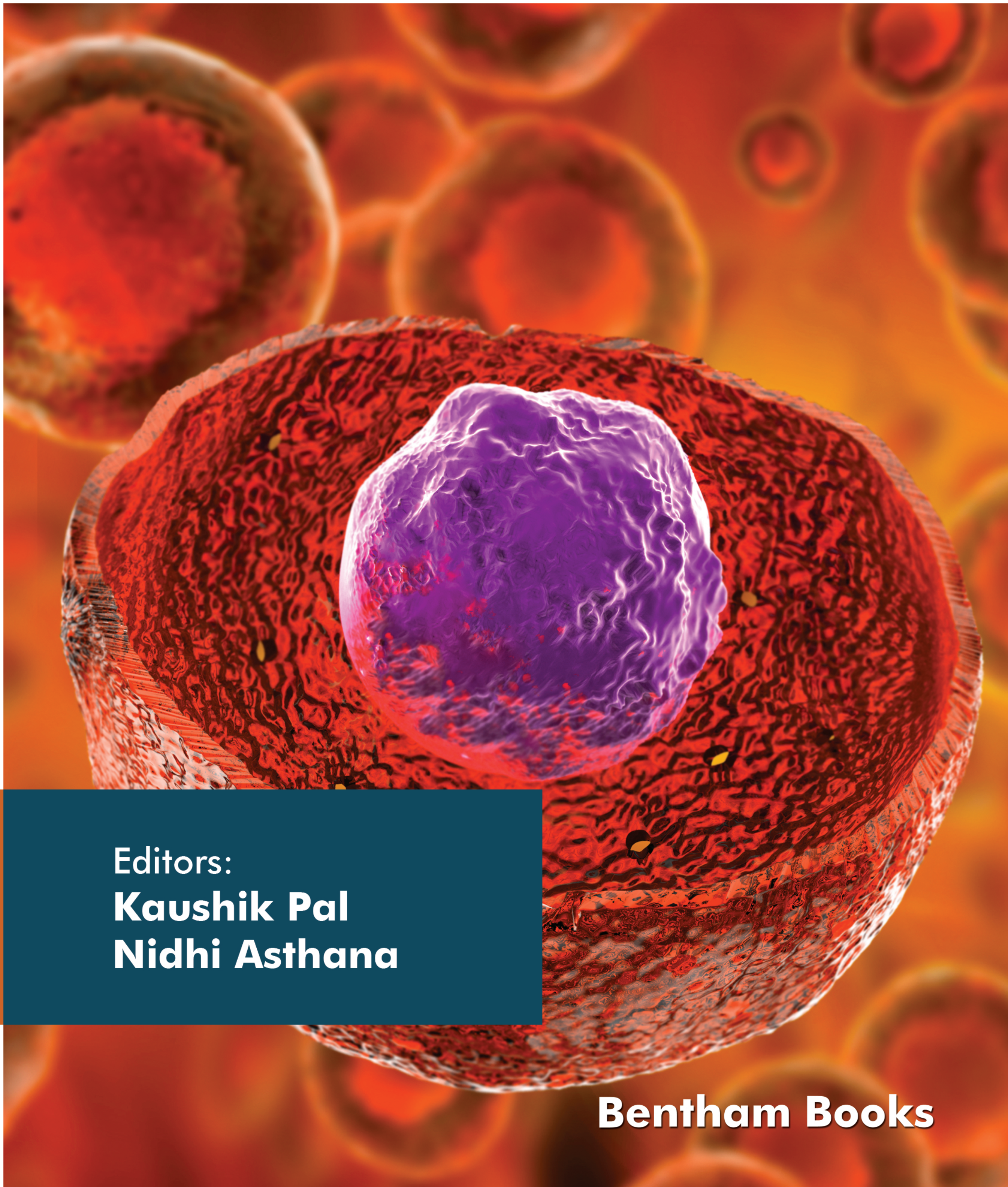
BIO-INSPIRED NANOTECHNOLOGY



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Bio-Inspired Nanotechnology

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PREFACE

The book 'Bio-inspired Nanotechnology', exploring recent breakthroughs of exciting novelties finding inter-and cross-multidisciplinary sciences is based on micro- to nanofabrication of bio-engineered nanomaterials, spectroscopic characterization, and promising avenues of eco-friendly products as well as sustainable potential applications at the industrial scale. This book comprises of nine significant chapters written in diverse fields of study on green chemistry, nanotechnology, advanced materials, nano-biotechnology as well as next-generation biomedical technology.

For the last several decades, there have been many projections on the future depletion of self-assembly of structural proteins that produce complex, hierarchical materials that exhibit a unique combination of mechanical, chemical, and transport properties. This controlled process covers dimensions ranging from the nano- to the macroscale. Such materials are desirable to synthesize integrated and adaptive materials and systems development of renewable energy technologies. On a different frontier, the growth and manipulation of materials on the nanometer scale have progressed at a fast pace. Selected recent and significant advances in the development of nanomaterials applications are reviewed in the entire book, and special emphasis is given to the investigations in Chapter 1 emphasizing an overview of supramolecular systems that are utilized as an effective technique in nanomanufacturing which enhances solubility, modification of surface properties, bioconjugation of nanoparticles fabrication which is the study of variations in non-covalent interaction to generate a nanostructural system with controlled characteristics. Chapter 2 deals with the significant fabrication of novel bio-nanocomposites by simple, cost-effective pathways using biocompatible, environmentally friendly zeolite and cellulose. The nanocomposites are water stable and have increased efficiency for adsorption. Moreover, these nanocomposites are more suitable for both Anionic and Cationic dyes. Chapter 3 illustrates polymer nanocomposites which are excellent materials with superior and exotic properties for biomedical applications. This chapter gives an overview of the major polymer-based composites reinforced with nanomaterials, their characteristics, fabrication techniques, and suitability in the biomedical field. The chapter gives an idea about research gaps in the material design and development, drawbacks, and challenges in *in-vivo* biomedical applications beneficial to researchers by giving an insight into novel materials suitable for further utilization in the biomedical era. Chapter 4 focuses on the conventional strategies based on nanotechnology which are being adopted in the biomedical field but having several disadvantages like severe side effects, toxicity, *etc.* From a future perspective, polymer nanocomposites have great potential in biomedical fields like tissue engineering, bone replacement or repair, dental applications and controlled drug delivery. The potential of biodegradable polymers in such applications is still under investigation. In the current scenario, polymer nanocomposites offer the combined merits of nanotechnology and the pros of biocompatibility and biodegradability to achieve the desired objective in biomedical applications. Chapter 5 illustrates modern-day nanomaterials of various kinds and morphologies and diverse methods of synthesizing them under top-down and bottom-up approaches are also discussed. Contributions of nanomaterials in some emerging technologies and industry sectors like the food industry, agricultural science, medicinal science and the power sector have been discussed. The need for awareness and risk management to combat the health impact of 'nanotoxicity' arising due to the rapid commercialization of nanomaterials is also mentioned. Also, Chapter 6 discusses the current discoveries in graphene-based materials in a variety of sectors as well as nanotechnology due to its hexagonal lattice and carbon atom arrangement. While, graphene nanosheets are excellent for usage as a 2D endorsement for applications of other nano-objects. Graphene-based nanocomposites are getting prominence in environmental and energy concerns in a variety of sectors. Chapter 7 deals with applications of nanotechnology in medicine which is relatively new, yet having a profound worldwide impact on biomedical research and public health. Nanomaterials possess several attractive features that permit them to perform physiological tasks such as multicolor imaging, identification of medical disorders, early diagnosis of diseases, delivery of therapeutics to target-specific organs, effective treatment of infections, increased bioavailability of drugs, and decreased side effects. Nanomedicine offers enormous opportunities in the near future and global efforts are underway to develop advanced smart nanomedical systems. Chapter 8 presents in-depth studies on the agricultural domain with which human civilization started and will carry on for survival. Since the growing population demands more resources from lesser area and time, bioinspired nanotechnology interventions like nanocarriers for fertilizer and pesticide delivery, soil and climate sensors and plant nanobionics to detect pollutants are the need of the hour. The strategies also have to be sustainable, in line with the UN SDGs as recalcitrant compounds have already posed significant damage to our planet. However, Chapter 9 explores the scenario of the utility of graphene nanotechnology that could be easily understood by its wide range of applications starting from energy storage devices to biomedical devices. Not only these, but graphene technology also provides purified water and air owing to its excellent physical, chemical, and mechanical properties. However, like any other technology, graphene nanotechnology has its limitations; advanced research is going on to overcome this. In the future, multifunctional graphene-based nanostructures with affordable cost will reach out to the common people. Remarkable strategies to employ assemblies of metal nanoparticles, organic-inorganic hybrid composite matrix, and carbon nanostructures in bioengineering conversion schemes are also illustrated in this book.

Thus, it may be clear to all readers that nanotechnology-enabled bio-inspired nanotechnologies are starting to scale up dramatically. As they become mature and cost-effective in the decades to come, biomaterials could eventually replace the traditional, environmental-unfriendly, fossils and improve the performance of the biomedical industry through the utilization of nanocatalysts in manufacturing materials with high durability. This book provides an overview of key current developments that direct future research attempts toward the utilization of such tailored nanostructures or hybrid nano assemblies will play an essential role in achieving the desired goal of cheap and efficient production.

The book contains information with evidence from academicians, scientists, scholars, and engineers. It illustrates the wide-ranging interest in these areas and provides a background to the chapters, which address the novel synthesis of high-yield nanomaterials and their biomaterials, graphene, polymeric nanomaterials, green nanomaterials, green polyester, nano-biotechnology, interesting response characteristics of exclusive spectroscopic investigation as well as extensive electron microscopic study, health care, environmental and plant biology, social, ethical, and regulatory implications of various aspects of green nanotechnologies based leading functional nanomaterials. Liable appropriate regulation alongside the topics indicates that the commercial production of manufactured novel composite materials can be realized. Furthermore, many brilliant discoveries and explorations are highlighted in the entire book that can modulate spectroscopic performances with technical excellence in the inter-and cross-multidisciplinary research of high competence.

Lastly, I would like to express my overwhelming gratitude to all the authors/co-editor for their excellent research contributions as well as peer-review, editing throughout this book. I would like to thank the entire team of Bentham Science Publishers for their efficient handling of this book at all harder stages of its publication. I am pretty sure and confident too that within a short interval, the book will be more popular in worldwide universities/institutes libraries and hopefully will achieve the highest citation in the coming years.

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CHAPTER 1

Design and Characterization of Smart Supramolecular Nanomaterials and their Biohybrids

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Abstract: Over the past few years, much effort has been taken to explore the applications of nanoparticle-based structures in different fields such as nanomedicine, molecular imaging, *etc*.. Supramolecular analytical methods have attracted researchers due to their chemical formula, flexibility, convenience, and modularity for the synthesis of nanoparticles. The incorporation of functional ligands on the surface of supramolecular nanoparticles helps to improve their performance in many areas. Fabrication of supra molecular materials with uniform size gives more advantages of using them in different fields. Characterization techniques like positron emission tomography imaging (PET), magnetic resonance imaging (MRI), fluorescence studies, scanning electron microscopy (SEM), and UV-Vis studies help to identify the molecular images and structure effectively. Supramolecular systems are used as an effective technique in the nano-design of supramolecular nano-systems. They enhance the solubility, modification of surface properties, bioconjugation of nanoparticles due to the supramolecular recognition properties, and supramolecular materials that are applied for the removal of targeted molecules. The designing process makes it able to function in complex matrices. This chapter discusses the design, synthesis and characterization of supramolecular nanostructures and their hybrids and also discusses their application in different fields.

Keywords: Characterization techniques, Complex matrices, Emulsion, Fluorescence studies, FT-IR studies, Functionalized nanomaterials, Hybrid nanoparticles, Ligands, Magnetic resonance imaging (MRI), Modularity, Nano precipitation nano structure, Nanoaggregation, Non-covalent interaction, Positron emission tomography imaging (PET), Scanning electron microscopy (SEM), Self-assembly, Stacking, Supramolecular nanostructure and UV-Vis studies.

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INTRODUCTION

Supramolecular chemistry is identified as the study of the chemistry of non-covalent interactions. Weak and strong interactions are used to form nanoassemblies and novel nanomaterials. These forms are applied in different fields such as biomedical, pharmaceutical and analytical. Supramolecular chemistry is the branch where studies emulated from nature are considered. Supramolecular chemistry is explored as the chemistry beyond the molecule. It is more studied due to the efficiency of the molecule to design the self-assembled systems. Generally, supramolecular complexes are highly dynamic with their complementary guest molecules [1]. They perform various weak and reversible non-covalent interactions such as ion-ion, pi-pi, hydrogen bonding, weak van der Waals interactions, *etc*.. [2]. Supramolecular systems are efficient due to their inherent modularity, assembling-dissembling to external stimuli and their reversible nature. Supramolecular chemistry is mainly based on the concept of self-assembly and molecular recognition [3]. This review details about the application of supramolecular systems, design, synthesis and characterization of supramolecular nanoparticles and application of SNP and its hybrids in different areas.

SUPRAMOLECULAR NANOPARTICLES (SNPS)

They are mainly classified into organic supramolecular nanoparticles and inorganic supramolecular nanoparticles. Supramolecular identification of nanoparticles can generate stable and packed 3D functional nanostructures. β-cyclodextrin (CD) acts in organic supramolecular nanoparticles as a natural host for guest organic molecules (ferrocene). It helps to form specific kinetically labile inclusion complexes. These guest-host complexes were applied in supra molecular system to assist the nanoparticle's assembly. The guest or host molecule was attached to the surface of different nanoparticles such as silica, gold, polystyrene, *etc*.. The major strength in supramolecular chemistry is the fine-tuning and binding strength of the related supra molecules. The reversible bonding of the nanostructure from the surface is very important for designing novel nanoarchitectures. It is gained by the assembly of supramolecular nanoparticles. SNPs are prepared from the mix of supra and polymer chemistry, and their interactions. While synthesizing drug delivery system, we first need to design biodegradable SNPs. It is recommended to use the combination of polymer and supramolecular chemistry which can be added with organic and inorganic NPs [4]. They help to tune the flexibility of polymer chains. In this way, they enable to design and synthesize different types of NPs. They are applicable in nanoimaging, nanomedicine, bioanalytical chemistry, *etc*.. These materials are biodegradable and biocompatible. SNPs are able to tune and optimize themselves for their targeted applications [5].

In SNP formations, the reactant biodegradable NPs are made up of monomers such as PLA, PA and copolymers. Many studies have reported the application of biodegradable SNPs for drug delivery. These SNPs are applicable in making stimuli-responsive multifunctional nanodevices [6]. As a result, polymer chains provide flexible branches which are functionally modified with macrocycles and connected by non-covalent interactions. They finally form polymeric supramolecular NPs that have wide applications in the pharmaceutical industry.

Hybrid Supramolecular Nanostructures

Biobased hybrid supramolecular nanostructures of inorganic and organic molecules have enough potential for the improvement of properties in electronic and energy transduction. They are highly applicable in the synthesis of nanomedicines and nanosensors [7] based fields. Nanoparticles used to synthesize hybrid supramolecular materials have vast functionalities on their nanostructure such as fluorescent, magnetic, metallic, drug-loaded, bioconjugates, *etc*.. [8]. Addition of metallic NPs into the polymeric NPs and supramolecular NPs makes them more efficient. It helps to enhance the intrinsic properties of each component which will tune the design and flexibility of the required nanoarchitecture .

STACKING OF SNPS

Generally, the assembly of molecules into 1D supramolecular polymer system leads to the formation of double sided motifs. These motifs are efficient in facial association and stacking through the combination of various non-covalent interactions. The assembly of these small molecular stacking motifs is led by their molecular structure and architecture. These assemblies can be varied by different factors such as pH, solvent polarity, salt concentration, *etc*. [9]. But some molecular stacking motifs are influenced by thermodynamic equilibrium.

DESIGN AND SYNTHESIS OF SUPRAMOLECULAR BIOHYBRID MATERIALS

Supramolecular compounds are generally classified into 2 types based on their synthesis and mechanism. They include materials synthesized from one-dimensional assembly of stacking and materials synthesized from the chain extension of oligomers of polymeric precursors by corresponding supra molecular recognition motifs. The design of supramolecular materials needs a special understanding of the characteristics of specific non-covalent interactions. This involves the interaction between different supramolecular motifs. In case of

CHAPTER 2

Biocompatible Composites and Applications

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Abstract: In this chapter, the low-cost, biodegradable absorbents are developed for wastewater treatment. At first, the modification of the procured nano ZSM-5 is executed by means of dealumination and ion exchange process to have de-laminated (D-ZSM-5), Cu-ZSM-5 and Fe-ZSM-5. Furthermore, cellulose nanofibrils (CNFs) are mixed with modified zeolites with varying concentrations (20 and 80 wt%) used for the fabrication of innovative composite films ((D-ZSM-5, Cu-ZSM-5 and Fe-ZSM-5). FTIR, XRD, BET_{CO2}, TGA, and SEM type of characterization techniques are used for the analysis of composites. The prepared composite films are exploited for cationic Rhodamine B (Rh6B) and anionic Reactive Blue 4 (RB4) dye elimination by the activity of adsorption. The effect of contact time, initial dye concentration and pH on the dyes' adsorption in aqueous buffer solutions is examined. The equilibrium adsorption data are estimated using Langmuir, Freundlich, and Temkin isotherm models. Langmuir isotherm is deemed to be the best-fitting model and the process (kinetics and mechanism) follows pseudo-second-order kinetics, yielding an uppermost adsorption capacity of 34 mg/g, and 16.55 mg/g which is comparable to plane CNF (8.7mg/g) and (0.243mg/g) for cationic Rh6B dye and anionic RB4 dye respectively. Maximum dye removal is observed for a higher amount of (80% ZSM-5) film. The study reveals that ZSM-5/ CNFs films can potentially be used for the removal of cationic and anionic dyes.

Keywords: Adsorption, Adsorption kinetics, BET, Cellulose nanofibrils, Dealumination, Dye modification, Freundlich, FTIR, Ion exchange, Isotherm models, Langmuir, Nanocomposites, Pseudo-first and second order, Reactive blue, Rhodamine B dye, Temkin, TGA, XRD, ZSM-5 zeolite.

INTRODUCTION

Material production is one of the major contributors to the water pollution. Various textile methods like dyeing, printing, and washing not only involve hazardous and non-biodegradable dyes, chemicals like nitrates, acetic acid,

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sulphur, naphthol, formaldehyde-based dye protective representatives, caustic soda-based soaps or enzymes, chromium compounds, but also a number of heavy metals namely copper, arsenic, lead, cadmium, mercury, nickel, cobalt, as well as hydrocarbon-based softeners. Moreover, clothing processes need a lot of water for cleaning of clothes as well as cleaning of related machines, and vessels. Thus, wastewater from the textile industry contains a number of poisonous pollutants which are observed to be very dangerous to the environment. Some of them can be removed by usual methods like chemical, photochemical and biological degradation, membrane filtration, coagulation/flocculation, precipitation, and solvent extraction, but some pollutants cannot be removed. However, it is due to toxicity, non-degradable, stable, and even carcinogenic nature of synthetic dyes, they are posing dismaying environmental problems [1, 2]. Hence, it is necessary to remove these effluents. Adsorption is an efficient, flexible, and economical method used for dye abstraction wherein hazardous dyes adsorb on the adsorbents like activated carbon, clay minerals, and porous materials [3].

Currently, nanocomposite adsorbents are being employed in line for their superior physical and chemical properties like surface area, morphology, structures, stability, and enhanced adsorption capacities [4]. In consequence, a number of nanocomposite adsorbents similar to graphite/Fe_3O_4 [5], CuO/NiO [4], graphene oxide/magnetite [6], hydroxyapatite/alginate [7], hydroxyapatite/chitosan [8], chitosan-based semi-IPN hydrogel composites [9], reactive resin composite [10], cobalt-hectorite composite [11], zeolite-activated carbon composite [12], carboxyl methyl cellulose–organo-montmorillonite composite [13], bentonite clay/activated charcoal mixture [14], carbon-mineral composite [15] and PVA/ATP composite [16] have been used for adsorption of several dyes.

Zeolites belong to a category of pioneering adsorbents due to their well-porous building. The honeycomb-like composition of zeolite comprises a three-dimensional frame, carrying a negatively charged matrix [17, 18]. The negative charge is well-regulated by switching with the neighboring cations. Moreover, the high surface area exhibited by the nano form of zeolites is the foremost advantage for a favorable adsorption process to occur [19]. In addition, zeolite is nontoxic and environment-friendly in nature. Hence, zeolite is preferred for the preparation of composites.

Moreover, materials with biological origin have been receiving growing attention due to highly ordered structure that ultimately makes up innumerable functional elements. The nature and structure of surface, morphology, and physical and chemical properties decide the unique properties exhibited by natural materials. Certain biological materials are of significant concern as they offer multi-functionality. It is well known that there are various composites of natural origin that exhibit extraordinary properties. Hence, the efforts are being made to develop novel composite materials with fascinating properties and functions for their commercial application in environmental protection by introducing bio-based material as reinforcing material.

Cellulose nanofibrils (CNFs), a natural polymeric raw material, have also proved themselves as very promising low-cost biocompatible products for environmental remediation [20, 21]. Moreover, their properties such as hydrophilicity, biodegradability, antibacterial nature, and dye adsorption ability make them more valuable. Urruzola *et al.* used bleached eucalyptus pulp as a raw material for the adsorption of toluene [22]. The synthesized organic cationic cellulose was used for controlling anionic amphiphilic drug and diclofenac sodium by Rodriguez *et al.* [23]. Khatri *et al.* used the cationic cellulose fibers for the color yield and dye fixation by dual padding method [24]. Wang *et al.* prepared the magnesium chitosan combination for the elimination of Congo red dye from an aqueous solution [25]. Krshni *et al.* used papaya stem fibers for the adsorption of hydrated methylene group [26]. Pei *et al.* reported the surface quantized cellulose nanofibers (Q-CNF) for adsorption water and anionic dye [27]. Sehaqui *et al.* used functionalized cationic CNF for the adsorption humic acid and removal of copper and positively charged dye [28]. Li *et al.* prepared the adsorbents created using maleic anhydride which improved cellulose fibers containing alkali-treated diatomite in support of the elimination of fundamental dyes, such as methylene blue and methyl violet [29]. Also, the nano celluloses and their phosphorylated derivatives have been used by Liu *et al.* for the adsorption of Ag^+, Cu^+ and Fe^+ from industrial wastes [30]. Literature review indicates that the CNFs, in functionalized or in modified forms, have been used for the adsorption or removal of dyes. However, the adsorption of dyes like Rhodamine B (Rh6B) and reactive Blue 4 (RB4) by CNFs has not been reported so far.

Furthermore, there are reports wherein zeolite/cellulose nanocomposites have been prepared using different methods like ionic liquid solvent [31], hydrothermal method [32] and colloidal method [33]. It has been shown that nano-cellulose–zeolite composites films, prepared by the colloidal method, yield high mechanical stability up to 10MPa [34] and these composite films, with high bending flexibility and surface area, can be employed for high thiol removal performance [35]. However, such composites have not been used for the removal of cationic and anionic dyes so far.

Hence, the present study deals with the modification of ZSM-5 zeolites and preparation of modified zeolite/CNF nanocomposites by solvent casting method. The structural properties of the tailored modified ZSM-5/CNF nanocomposites have been studied by FTIR, XRD, TGA, BET and SEM analysis. These

CHAPTER 3

Polymer Nanocomposite Technologies Designed for Biomedical Applications

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Abstract: The combination of polymer composite technology and nanotechnology leads to the design of polymer nanocomposites. They represent a novel alternative class of materials to traditional composites with versatile properties which are suitable for biomedical applications. The addition of nanofillers to polymer composites enhances their mechanical and biological characteristics. The enhancement in various properties depends on the polymer matrix, filler, and matrix-filler interaction. The major issue faced in biomedical research during product development is the lack of biocompatibility and biodegradability. The primary factor that has to be considered for composite development is the proper choice of materials. There is a growing demand for the design of personalized medicine with the outbreak of many chronic ailments and genetic disorders. The properties of polymer nanocomposites can be customized for various biomedical applications. The characteristic features of supramolecular nanocomposites which act as smart materials with tuned properties can be exploited for tissue engineering, responsive drug and hormone delivery, regenerative medicine, bioimaging, ocular, dental and orthopedic applications. Many hybrid biopolymer composites which exhibit promising biomedical applications are developed by researchers. Their properties can be tailored for making biomedical devices also. This chapter highlights a brief but focused overview of biomedical applications of bio-based polymer nanocomposites, carbon-based polymer nanocomposites, metal-organic framework/polymer nanocomposites, shape memory polymer nanocomposites, hydrogels, self-healing polymer nanocomposites and stimuli responsive polymer nanocomposites.

Keywords: Biomedical applications, Carbon-based polymer nanocomposites, MOF/polymer composites, Polymer-nanocomposites, Shape memory polymers, Targeted drug delivery.

INTRODUCTION

Polymers are macromolecules which represent a fascinating class of materials that are formed by the interlinking of thousands or millions of repeating chemical enti-

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ties called monomers. They are present everywhere and have become an inevitable part of human life. Many natural materials are polymers. They range from natural biopolymers like DNA, proteins, *etc.* to synthetic commonly used polymers like polyesters, polystyrene, *etc.* Their unique and versatile properties make them irreplaceable and inexorable among the materials. The interaction between monomers imparts different characteristic properties to polymers. Unlike metals, polymers are highly resistant to chemicals and thus they can be used in corrosive environment. Their excellent lightweight property makes their application highly competitive against metals. Many polymer composites possess remarkable strength and durability compared to their metal counterparts. They are basically nonconductors of heat and electricity. Other characteristic features of polymers which make them the material of 21^{st} century are their low cost, strength, elasticity, stiffness, resilience, toughness, ease of processing and modification. The properties of individual materials are enhanced by the combination to form a class of material called composites, where the constituents having divergent physical and chemical properties, formulate themselves as matrix and reinforcement materials. The presence of reinforced or strengthening materials improves the properties of matrix materials for the optimum combination of constituents. Thus engineered composites for different applications can be synthesized by a variety of combinations of constituent materials. Now this is the era of nanotechnology which creates wonders in enhancing the characteristic properties of materials which contribute to their exotic applications. When at least one dimension of the composite material is in the nanometer range, it forms a nanocomposite. They can be classified depending on the matrix materials as Ceramic Matrix Nanocomposites, Metal Matrix Nanocomposites and Polymer Matrix Nanocomposites. Compared to micro composites, nanocomposites have a complicated structure and exceptional features. In this chapter, a focused review of the properties of Polymer Nanocomposites (PNCs) and their recent advances in biomedical research are discussed.

Polymer Nanocomposites

The reinforcement of nanoscale components or nanofillers into polymeric matrix leads to the formation of a homogeneous phase of polymer matrix nanocomposite or simply polymer nanocomposite. Nanofillers have revolutionized the polymer modification field. They are the ultimate reinforcing agents due to their large surface area and high interfacial activity, which lead to extensive interphase interactions. They can bring about much higher reinforcement compared to conventional fillers used in polymer modification.

The properties of the polymer composites depend on the fillers dispersed in the polymer matrix. Their properties can be suitably tuned by properly selecting the polymer, filler, synthesis methods and additives used for increasing dispersion. These components develop effective interactions between the polymer matrix and the nanofiller which are responsible for the property improvement in nanocomposites. Fig. (**1**) depicts the general plot to represent enhancement in the mechanical property of PNC compared to the conventional polymer, as a function of the concentration of nanofiller. The presence of nanofiller in the polymer matrix enhances its properties for an optimum filler content, which depends on the matrix and filler. Higher concentration of nanofillers leads to improper dispersion and aggregation that adversely affect their properties [1].

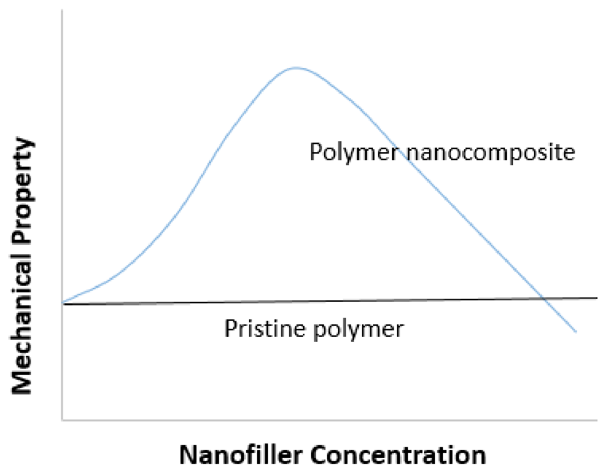

Fig. (1). General plot to represent enhancement of property of PNC compared to conventional polymer.

Many nanostructured materials like inorganic and organic nanoparticles, magnetic nanoparticles, metal-organic frameworks, silicates, carbon-based nanomaterials like carbon nanotubes, graphene and their derivatives are compatible with polymers to form PNCs. Good intercalation chemistry between silicates and polymers and the abundance of nanosilicates make polymer-layered silicate nanocomposites popular. The formation of intercalated and exfoliated polymer silicate nanocomposites compared to conventional composites is illustrated in Fig. (**2**). It shows that proper dispersion of filler in the matrix is ensured in the formation of PNCs which are responsible for their property enhancement.

CHAPTER 4

Novel Polymer Nanocomposites: Synthesis, Designing and Cost-effective Biomedical Applications

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Abstract: The design of materials for various biomedical applications is truly challenging since it demands exceptional characteristics such as biocompatibility, biodegradability, non-cytotoxicity, adequate strength, *etc.* Several strategies have been developed for the synthesis of nanoparticles based on chemical methods. However, the toxicity limits their applications in biological systems. So researchers are looking for materials that can fulfill green criteria in the sense that they should be renewable, harmless to human health, and environment friendly. Recently, the evolution of nanomedicine led to explore the possibilities of different types of nanomaterials in various applications. Nanoscale polymeric materials and polymer nanocomposites have already proved their versatility in various biomedical applications. This chapter presents a brief overview of the potential of biobased nanomaterials and nanofillers such as metal and metal oxide nanoparticles, hydroxyapatite, nanotubes, graphene, chitin whiskers, lignin, nano cellulose, *etc.* and their pros and cons when used in the biomedical field. Bio-based polymers are promising candidates for the next generation nanocomposite materials due to their multi-functionality, renewability, low toxicity and excellent biocompatibility. The chapter begins with the state of the art including the recent developments in the biomedical field and finally, the challenges and future potential of various nanoparticles and polymer nanocomposites are also discussed.

Keywords: Biomedical applications, Biopolymers, Chitosan, Nano cellulose, Nanoparticles, Polymer nanocomposites.

INTRODUCTION

Evolution of nanoscience and nanotechnology is one of the revolutions in pharmaceutical and biomedical research owing to the attractive features for drug delivery, vaccine formulation, biosensing, *etc.* The area dealing with the applicat-

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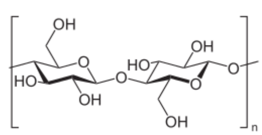
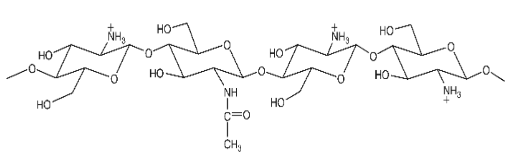
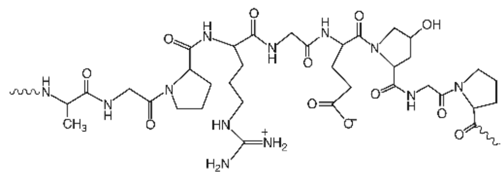
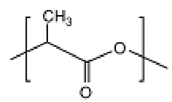
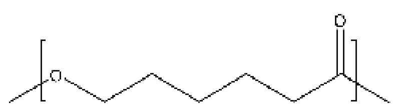
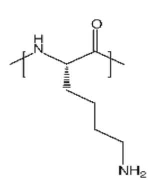
ion of nanomaterials for the medical diagnosis, treatment and prevention of diseases is termed nanomedicine [1].

Polymers have multifaceted applications in the biomedical field due to their versatility in properties and biological performance. The first and foremost requirement for a polymer to be used in the biomedical field is biocompatibility which is the ability of a material to fulfill the desired purpose without leaving any harm to the cells or tissues [2]. Biopolymers are sustainable resources. Biocompatible natural polymers used in biomedical applications are chitosan, chitin, cellulosic polymers, starch, other protein-based polymers, lignin, aligante, *etc.* and biocompatible synthetic polymers used for such applications include polylactic acid (PLA), poly (ε-caprolactone) (PCC), poly(lactic-co-glycolic acid) (PLGA), poly (p-dioxanone) (PPDO), *etc.* The benefit of using natural biomaterials is that they get degraded gradually and subsequently tissue regeneration takes place. Several bio-based nanomaterials have been widely used in tissue engineering scaffolds, biomedical implants, drug delivery applications, medical diagnostics, *etc*. [3 - 5]. Some of the common biopolymers, their advantages and their biomedical applications are listed in Table **1**. The potential of biocompatible polymers for the design of nanomaterials is the topic of active research for the past few years.

Table 1. Commonly used biopolymers and their advantages and applications.

Biopolymer	Structure	Advantages	Field of Application
Cellulose		The most abundant natural organic polymer having high, high surface area and biodegradability	Drug delivery systems, pharmaceutical coating processes, tissue engineering, wound dressings, medical implants, cartilage replacements, gelling agents *etc*. [6, 7].
Chitosan		The biodegradable and biocompatible polymer has attractive film-forming properties.	Drug and vaccine delivery, tissue engineering, antimicrobial agent, wound healing *etc*. [8, 9].

(Table 1) cont.....

Biopolymer	Structure	Advantages	Field of Application
Collagen		Able to carry any component because of its three-dimensional network-like structure.	Sponges for burns and wounds, protein delivery, drug delivery, tissue engineering including bone substitutes, making artificial blood vessels, valves *etc.*, for skin replacement, ophthalmic application [10, 11].
Poly lactic acid (PLA)		Biodegradability, renewability, and high transparency	Tissue engineering, drug carriers, in cancer therapy, cardiovascular implants, skin and tendon regeneration, in dentistry [12, 13].
Poly (ε-caprolactone) (PCL)		Biocompatibility Biodegradability, cheap and readily available	Used for synthesizing scaffolds for various tissue engineering applications. Used for various implantable biomaterials [14, 15].
Poly(L-lysine) (PLL)		Biodegradability, non-antigenicity and biocompatibility.	Antibacterial applications, gene delivery, drug delivery, protein delivery, bio-sensing, bio-imaging, tissue engineering [16, 17].

CHAPTER 5

An Emerging Avenue of Nanomaterials Manufacturing and Prospectives

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Abstract: Nanotechnology is a perfect blend of science, engineering, and technology conducted on a nano-scale. Few nanomaterials can occur naturally, however, in recent times, we are interested in engineered nanomaterials which can be manufactured according to their applicability in a lot of commercial products and processes. For the synthesis of new nanomaterials, scientists mostly opt the bottom-up methods which are capable of offering various kinds of self-assembly of nanoscale species. Parallelly, top-down methods are also being investigated to yield desired nanomaterials and nanopatterns through state-of-art modern techniques like lithographic ablation and chemical etching. In this chapter, after providing an introduction to nanotechnology and nanomaterials, the various methods of nanomaterial synthesis were discussed. Nanotechnology is now being explored vastly to reach the next generation phase of many technologies and industrial sectors. Contributions of nanomaterials to some of such emerging technologies, like the food industry, agricultural science, medicinal science, and the power sector have been briefly overviewed. The rapidly developing sectors involving ultrafine nanoparticles introduced mankind to their hazardous side too. To avoid nanotoxicity, the awareness and related risk management approach are also a matter of utmost importance.

Keywords: Nanomaterials, Nanotoxicity, Power sector, Synthesis, Technologies.

INTRODUCTION

Although the terms ‘nanomaterial’ or ‘nanotechnology’ are not much old, there are evidence and documentation of the utilization of these ultra-fine materials by ancient human civilizations in Egypt, China, and Rome dating back to 1300 BC - 300 AD. Dr. Norio Taniguchi from the Tokyo University of Science, Japan, proposed the concept of nanotechnology first time at the International Conference on precision engineering. He explained the importance of preciseness and a nano-

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scale (1 nm = 10^{-9} m) material that implants enhanced and unique properties than the bulk amount of the same material. In this 'nano scale' material or 'nanomaterial', at least one dimension of the material is expected to be in the range 1 to100 nm. The nanomaterials can be biological, inorganic, or organic structures with various dimensions, sizes, shapes, and compositions.

For the last few decades, nanomaterials are dominating nearly all interdisciplinary industrial sectors ranging from agricultural, food industry, and renewable power sector, to medicinal sciences, and so on. The R and D sector on the engineered nanomaterials has a potential impact on the global economy right now. In this chapter, the various synthesis routes for nanomaterials have been discussed and their design and application in various emerging fields have been briefly explained. The desired awareness and related risk management approach associated with the relatively new term 'Nanotoxicity' have also been discussed in brief. The unique properties of nanomaterials hold the key to the enormous potential of technological progress in the future. But to reach that summit for mankind, proper scientific studies dedicated to the exploration of design, production, characterization, and technology-based utilization of nanomaterials are of utmost importance.

NANOMATERIALS AND NANOTECHNOLOGY

The nanomaterials differ considerably in their physical and chemical properties from bulk materials. As the size and surface chemistry of nanomaterials control their optical properties, they have been found to drastically differ from bulk solids. The properties of nanomaterials are (i) very high surface/volume ratio and surface energy, (ii) enormous mechanical strength and microhardness, (iii) large specific heat, (iv) large thermal expansion, (v) high catalytic activity, (vi) enhanced self-diffusion, (vii) high magnetic susceptibility and (viii) high sintering rate. The nano-dimensional materials possess a 'quantum size effect'. The term can be described as a change in the electronic properties of solids triggered by a considerable reduction in the size of particles than the bulk. High surface-to-volume ratios offer more subtle and better performance as catalysis, gas sensors, *etc.* Pure and bimetallic nanoparticles, various metal oxides, mixed metal oxides, chalcogenides, salts (*e.g.*, carbonate), and semiconductor nanomaterials, are being explored extensively for their enhanced mechanical, electrical, magnetic, optical, chemical, and several other properties. In the nanocomposite, nanomaterials or nanoclusters can be dispersed in the ceramic or polymeric matrix or can be a part of a bigger metallic cluster. The matrix usually is larger in dimension than the nanoscale. Unlike bulk materials, the properties of nanomaterials can be tuned with the help of nanoengineering. The ultimate purpose of skillful designing, tuning, and synthesis of desired nanomaterials for emerging technologies is to obtain efficient, economic, and faster devices with greater functionality through a sustainable approach including the economy in energy utilization and raw material consumption. The various nanomaterials can be classified depending on the types of materials, composition, morphology, and overall dimensionality (Fig. **1**).

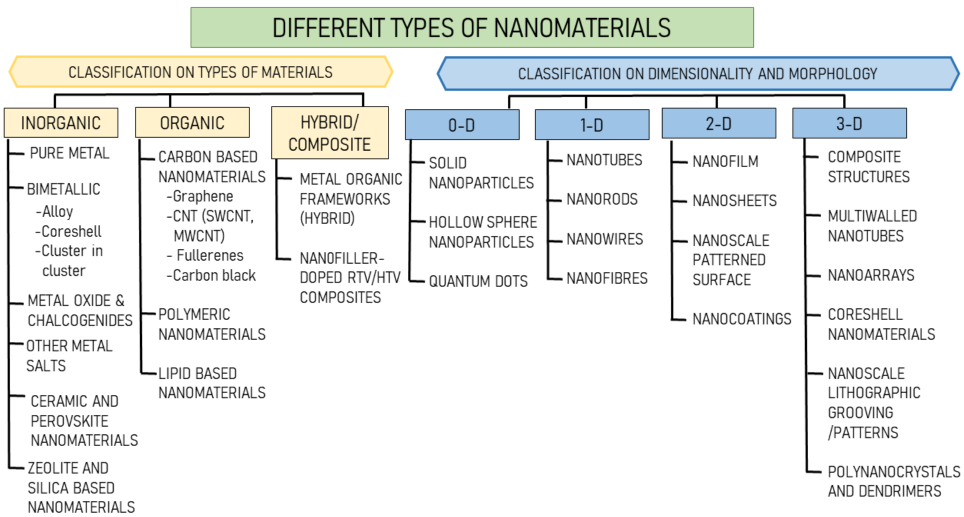

Fig. (1). Different types of nanomaterials.

Nanomaterials may be inorganic, organic, or hybrid/composite of both. Inorganic nanomaterials can be metallic (Au, Ag, Fe, Co, Zn, *etc.*) or bimetallic nanomaterials (Pd-Au, Au-Ag, *etc.*). Depending on the distribution of the metals in the cluster in bimetallic nanomaterials, (i) metal atoms can be distributed evenly and form an alloy, or (ii) one metal fills the core while the other coats the surface of the particle (core-shell) or (iii) the nanoparticle can hold different clusters of component metals/materials together (cluster in a cluster). Metal oxide and chalcogenide nanoparticles are common in nanotechnology-related research. Nanomaterials made of oxides of various metals (Ti, Fe, Cu, Co, Zn, Mg, Mn, Ni, *etc.*,) and metal chalcogenides (CdS, CdSe, CdTe, ZnS, ZnSe, GeS, GeSe, HgS, *etc.*) have been reported extensively in the literature regarding their synthesis and application scenarios. The nanomaterials of other metal salts like carbonate or sulfate are rather less reported; a few examples include barium sulfate, calcium carbonate [1], *etc.* Ceramic, perovskite, and double perovskite nanomaterials ($BaTiO_3$, $SrTiO_3$, Gd_2FeCrO_6, La_2NiMnO_6, *etc.*) exhibit many useful semiconducting, magnetic, insulating, and superconducting properties [2]. Zeolite and mesoporous silica nanomaterials (silicates and aluminosilicates) are another

CHAPTER 6

Current Research Trends of Graphene Nanotechnology

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Abstract: This revolutionary carbon nanomaterial has the potential to be used in a wide range of applications. Graphene was discovered to be the first two-dimensional crystalline carbon nanomaterial, as well as the most flexible, strongest, and toughest. The widespread application of graphene demonstrates its huge potential in a variety of industries, along with photovoltaic cells, electrochemical, optoelectronics, electronics, microelectronics, intelligent gadgets, extensible supercapacitor electrodes, aerospace, smart sensors, and analytical chemistry. The commercialization of graphene will be vital to the future of an industrially viable method of producing and processing graphene. Nanotechnologies based on graphene are gaining prominence in environmental and energy applications. Graphene has exceptional physicochemical properties, including high surface area, chemical resistance, heat capacity, mechanical characteristics, and charge transport. It might be used in environmental remediation, water purification, and desalination filters, as an electrocatalyst for contamination sensing. A broad literature collection will also be provided on graphene technology, including graphene characteristics, production processes, and uses. Graphene is the most popular carbon-based material, with excellent unique advantages such as high electrical conductivity, high tensile strength, high thermal conductivity, high carrier mobility, and transparency, making it a compelling candidate for a variety of applications such as sensors, transistors, energy storage, water purification membranes, solar cells, and elastomers. Although development in graphene-based nanomaterials for devices is encouraging, certain important issues such as long-term stability, toxicity, and environmental impacts remain unresolved. In this chapter, we assess recent advances in graphene research and applications and also attempt to predict where the field might go in the future.

Keywords: Carbon nanomaterial, Environmental remediation, Energy conversion, Graphene-Based nanotechnologies.

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INTRODUCTION

Graphene, a two-dimensional monolayer of sp^2 bonded carbon atoms with something like a hexagonal compacted crystalline lattice, was reportedly discovered in 2004.

It is currently expected to surpass all other carbon allotropic forms in material engineering and innovation [1]. Graphene serves as the foundation for various graphitic materials. In 1 mm of graphite, there are approximately 3 million layers of graphene. Nanographene is created by selectively eliminating hydrogen atoms from organic carbon and hydrogen molecules, a process known as dehydrogenation. Because graphene has a high surface area per gram of 2630 square meters, you could cover an entire soccer field with less than 3 grams. Graphene is the fundamental building block for any graphitic material.

Graphene also constitutes a new and unique class of materials that are only one atom thick, termed two-dimensional (2D) materials since they only expand in two aspects: length and width. The material is particularly appealing for the manufacture of 2-dimensional van der Waals heterostructures, which could be accomplished by hybridizing graphene [2].

Graphene possesses several remarkable properties, including excellent mechanical strength, improved thermal conductance, outstanding opacity, a massive high surface area, and efficient charge transport [3, 4]. Graphene as well as its variants, including graphene oxide (GO) or reduced graphene oxide (rGO), have attracted attention in the fabrication of new high-performance graphene-based materials for a broad array of applications. Sensors energy storage systems [5, 6], and photocatalysts with higher solar-to-fuel energy conversion [7, 8], are some of the applications. Graphene and its derivatives might be used in Li/Na batteries, hydrogen fuel, supercapacitors, and photosensitizers in photovoltaic panels. Graphene is an effective material for the remediation of environmental toxins such as inorganic [9, 10] and organic [11, 12].

STATUS OF GRAPHENE IN NANOTECHNOLOGY

Many scientists have termed graphene the "wonder substance" of the 21st century. The carbon-based polymer is nearly 200 times stronger than steel and bendable, extensible, virtually translucent, and extremely conducive to heat and electricity. Graphene is nothing more than a thin sheet of carbon atoms bonded in a hexagonal lattice, although it is extremely small and compact, making it an attractive material for nanotechnologies. Because of its interesting features and immense promise for a wide range of applications, graphene has attracted significant attention in recent years [13 - 16]. Its applicability in cost-effective and energy-efficient or energy-related products, including photovoltaic cells, Li-ion secondary batteries, and an ultracapacitor, has piqued the interest of many. Therefore, for real-world applications, graphene must be widely available. When it comes to the realistic appraisal of graphene, its availability and processability are the bottlenecks [17 - 19]. When it comes to the production and use of bulk graphene sheets, one of the most difficult challenges is reducing the stronger intermolecular van der Waals energies of graphite π -stacked layers [20]. Several physical or chemical procedures have already been proposed over the years for producing single or multiple layers of graphene.

SYNTHESIS AND PROPERTIES OF MATERIALS BASED ON GRAPHENE

Graphene Synthesis

Graphene may be coiled into zero-dimensional fullerenes, or multiplied and layered into 3D graphite as the essential building element of carbon nanomaterials. Top-down selection of the basic material for graphene and graphene-based nanomaterials may be done using these graphitic materials, as shown in Fig. (**1**).

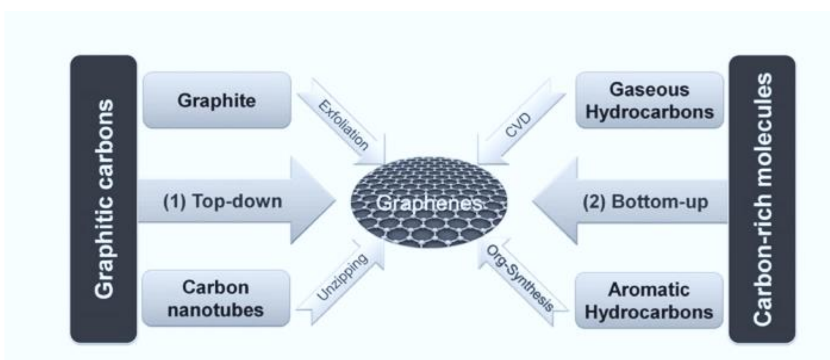

Fig. (1). Models of chemical strategies for producing graphene from various carbon sources (Reused with permissions from 21).

The oxidative exfoliation of graphite is a common top-down chemical way of generating single graphene sheets. Most of the oxidation has taken place using the Brodie, Staudenmaier, and Hummers techniques [21 - 26]. Graphite oxide is first reduced to graphene oxide by thermal treatment and simultaneous elimination of the oxygen-containing groups, or it is separated into single graphene oxide sheets

CHAPTER 7

Nanomedicine Technology Trends in Pharmacology

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Abstract: Nanotechnology deals with materials that are 1–100 nm in size. Nanomaterials are prepared in different ways such as physical, chemical, and biological methods. They exhibit fascinating features that allow them to perform numerous physiological tasks. They have higher surface area to volume ratios and show typical nanoscale quantum confinement characteristics. They play a critical role in biomedical research. They're quite versatile and used in a variety of medical applications. The demand for nanomedicine drugs with improved performance and reduced toxicity has been steadily increasing in recent years. Nanomedicine is the new area of nanoscience and nanotechnology. Pharmaceutical nanosystems are classified, synthesized, and characterized using procedures based on their size, shape, and functionality. This book chapter focuses on recent trends of nanomedicine technology in pharmacology, particularly on the application of nanomaterials in medicine. Antibacterial characteristics, multicolor medical imaging, disease diagnostics, medication administration, vaccines and biomolecules (peptides, proteins, and genes), therapies, cancer treatment, tissue engineering, and clinical aspects are discussed. Advancements in nanomedicine technology will not only aid in the early diagnosis of infectious and viral disorders, but also in the treatment of infections such as Alzheimer's disease, tuberculosis, and Parkinson's disease. The benefits and constraints of commercializing nanomedicine technology products for pharmacology applications, as well as the hazards and obstacles in developing nanomaterials for medical research are highlighted in this chapter.

Keywords: Drug delivery, Nanomedicine technology, Nanomaterials, Nanotherapeutics, Pharmacology.

INTRODUCTION

Nanotechnology is a discipline of science and engineering that deals with the design, manufacturing, analysis, and use of extremely small matter and equipment

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on scales ranging from 1 to 100 nanometers (1 nanometer or 1 nm = 10^{-9} m) [1]. Nanotechnology has grown rapidly in the last two decades, and it is currently in the explosive phase of development [2 - 4]. Nanotechnology is an interdisciplinary field that uses physics, engineering, chemistry, biology, and medicine to solve health problems. The term "nanomedicine" refers to the application of nanotechnology in medicine [5]. Rapid breakthroughs in nanomedicine have changed science and technology in the twentieth century [5]. It opened up a myriad of new possibilities in medical science and public health [2]. Nanomedicine technology is used for the prevention, diagnosis, and treatment of diseases [5, 6]. Imaging and diagnostics, drug delivery systems, tissue engineering, bone implants, and pharmacological therapies are all consequences of nanomedicine technology [5, 7]. It also focuses on the advanced treatment of musculoskeletal disorders, cancer, diabetes, viral and bacterial infections, and illnesses (cardiovascular, neurodegenerative, and psychiatric diseases) [5, 8].

Nanomedicine technology is rapidly growing due to financial support from federal agencies, businesses, and academic institutions [9]. In addition to the introduction of several new research and development (R&D) programs, many new nanomedicine patents have been submitted in recent decades [10, 11]. The National Nanotechnology Initiative (NNI) was established in 2001 as a multi-agency program with financing from the US government [9, 12, 13]. There is a huge rush of activity in nanomedicine technology research centered on NNI, particularly from the pharmacology projects of the National Institutes of Health (NIH) [13]. NNI funds nanomedicine technology projects that promote fundamental infrastructure, academic education, research and development, and commercialization of nanomedicine products. The NNI budget request for nanotechnology research and development in 2006 is $1.05 billion [9, 12]. The ANC (Alliance for Nanotechnology in Cancer) program at the NCI (National Cancer Institute, USA) had developed eight CCNEs (Centers of Cancer Nanotechnology Excellence) and twelve CNPPs (Cancer Nanotechnology Platform Partnerships) to encourage nanomedicine technology research and development [10, 14]. The National Heart, Lung, and Blood Institute's PEN (Program for Excellence in Nanotechnology) also promotes nanomedicine research [10].

Nanomedicine technology aims to identify and cure diseases in patients in a timely and accurate manner. It also encompasses a wide range of other advancements, including enhancements to existing techniques as well as the development of new instruments and capabilities [10]. The synthesis and characterization of numerous nanomaterials (NMs), as well as their preclinical uses, were demonstrated using nanomedicine technology R&D approaches [15]. In addition, nanomedicine techniques allow the regulation of vaccine or drug properties such as blood pool retention periods, solubility, regulated release (for shorter/longer duration), and target-specific drug delivery [10]. Furthermore, quantum confinement effects and different surface area to volume (S/V) ratios of NMs can be used in many ways. NMs and nanodevices have a very precise impact on the body at the molecular and cell/tissue levels. NMs are used in a variety of cellular and tissue-specific drug delivery applications to achieve optimum medical efficiency with minimal side effects [2]. However, before being commercialized, nanomedicine products must overcome hurdles such as durability, cost, large-scale manufacturing, and environmental effects.

In this book chapter, classification, synthesis, characterization, and antibacterial properties of NMs such as liposomes, micelles, polymeric NPs, emulsions, dendrimers, quantum dots, carbon nanotubes, *etc.*, as well as medical applications of NMs in molecular imaging, disease diagnosis, drug, and biomolecular delivery, therapeutics, and tissue engineering are discussed. Finally, the advantages and disadvantages of clinical nanomedicine, obstacles, hazards, and prospects of nanomedicine technology in illness detection and therapies are outlined.

NANOMATERIALS AND NANODEVICES

Nanotechnology - History

The word 'nano' comes from the Greek language and means dwarf or small. One nanometer (1 nm) is the length of six carbon atoms or ten H_2O (water) molecules put together. A human hair is roughly 80,000 nm wide, while a red blood cell is about 7000 nm wide. Ancient people employed NMs in artworks (Lycurgus cup, stained glass windows, ceramic glazes, Renaissance ceramics, *etc.*) and weaponry ('Damascus' blade), but they were unaware of the science and technology behind them. In 1959, R. Feynman delivered a well-known lecture on “There's Plenty of Room at the Bottom” and he was the first to lay out the ideas of nanotechnology [16]. Feynman anticipated the power of nanotechnology to manipulate matter at the atomic/molecular level, as well as its ability to examine and control the structure and behavior of materials at nanoscales. In 1974, N. Taniguchi coined the term “nanotechnology” referring to its ability to accurately engineer materials at nanoscales [17].

The semiconductor industry was the driving force behind miniaturization, intending to build smaller, faster, and more intricate electronic components on silicon microchips based on Moore's law, which predicts that the total number of transistors on microchips will double every two years [18]. In 1981, H. Rohrer and G. Binnig invented the scanning tunneling microscope (STM) for imaging material surfaces at atomic scales and creating nanostructures using atoms and molecules [19]. The tunneling current is used selectively by the STM device to

CHAPTER 8

Agricultural Nanotechnologies: Future Perspectives of Bio-inspired Materials

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Abstract: Bio-inspired designs have been used by humankind in understanding and modelling novel materials which have applications in diverse fields like disease diagnostics, drug delivery, agriculture, energy storage, industry, *etc.* Superhydrophobicity, directional adhesion, structural colour, self-cleaning, antireflection, *etc.* are some of the useful attributes for which we have relied a lot on nano level biomimetics. Bioinspired nanolevel designs have been explored in the field of agriculture too. Such nanomaterials and nanodesigns have been used to increase crop yields. They also find uses in fertilizer application and replacement of many harmful chemical pesticides, which are generally overused. Increasing population, increased longevity of people and the urgent need for sustainable environment have led to a dire need for exploration and adaptation of such novel technologies which can help in feeding the growing population. Nanoscale products and technologies can also help in reducing the accumulation of excess fertilizers, pesticides, *etc.* in soil, which can go a long way in cleaning up the environment. The current attempt is intended to portray the latest developments and future possibilities of bioinspired NT in diverse fields of agriculture like synthesis and delivery of novel pesticides and fertilizers, nanocarriers for gene delivery, sensors to monitor and assess soil conditions, plant pathogen detection and plant nanobionics to detect pollutants.

Keywords: Agriculture, Biosensors, Dendrimer, Gene delivery, Liposome, Nanobiosensors, Nanocapsule, Nano-coating, Nanodesign, Nanofertilizers, Nanofiber, Nano fungicides, Nanogel, Nano herbicides, Nanopesticides, Nanosphere, Nanobionics.

INTRODUCTION

The properties exhibited by a material vary drastically when converted to nanoforms, compared to its conventional forms. With increasing advancements in

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the equipment available for the study of such nanoscale particles, scientists grew curious to find applications for these in diverse domains. Bioinspired nanolevel designs have been explored in agriculture too. Agricultural yields are influenced by numerous environmental factors, including abiotic constraints (soil components, pH, physicochemical and biological properties and climatic-induced stresses) and biotic factors (beneficial organisms, pests and pathogens). In terms of limiting agricultural production, soil fertility is second to pest and pathogen-associated diseases. Climate change too has a significant impact on the adaptive potential of plants and associated pathogens populations [1]. Over a billion people around the globe have been estimated to be facing varying degrees of starvation due to insufficient nutritional intake and the unavailability of staple grains. In order to counteract the loss of yield, adequate soil health, and fertility management, climate-friendly farming and precise early determination and control of pathogenic microbes become essential [2]. Thus, it is imperative to meet the projected 70% increased production demand by 2050 to feed the rising population (9 billion by 2050) and livestock [3]. Fertilizers, pesticides, herbicide formulations and delivery, nano biosensors in soil, climate and pathogen management, gene transfer, and other aspects of nano-enabled agriculture shall be covered in this chapter.

NANOMATERIALS TO IMPROVE PLANT GROWTH

Nanomaterials in Fertilizer Formulation

Nano fertilizers (NF) circumvent many potential problems posed by conventional fertilizers. Limited efficacies are caused by issues such as low uptake, leaching, and low conversion to bioavailable forms, as well as a higher quantity of chemicals put into the soil, resulting in soil deterioration and increased expenses for farmers. Various formulations of NF have been tried to address these problems in a very efficient manner. The use of NT in fertilizer production can be seen as an advancement in the field of crop management and “smart farming”. The most crucial and prospective advantage of NFs over conventional fertilizers is that they are environmentally benign due to the reduced quantities administered. As a result, leaching, runoff, and gas emissions into the atmosphere are all reduced. Nutrients are incorporated alone or in combinations onto adsorbents with nano-metric diameters to create NF (1-100 nm) [4]. These are classified into nanoscale fertilizers, nanoscale additives, and nanoscale coatings based on the type of formulation. Nanoscale fertilizers are conventional fertilizers rendered as nanosized particles. Fertilizers with nanoscale additives contain a nanomaterial supplement in the traditional formulation of fertilizer.

Multiple methods are used to obtain NPs, including physical, chemical, and biological. Methods like chemical vapour deposition, chemical precipitation, sol-gel, and electrodeposition are widely used [5]. However, the biological route for the production of NPs is the safest way to increase agricultural production while preserving the environment. The physical method, also known as the top-down method, involves milling zeolite or a comparable substrate to nanoscale using modern ball-milling equipment. The adsorption of nutrients takes place on nano-sized substrates/carriers. Surfactants, for example, are utilized as stabilizers to prevent agglomeration during adsorption. Surfactant modifications to zeolite are utilized to improve its carrier efficiency, and surfactant-modified zeolites (SMZ) are used to successfully transport anionic nutrients (NO_3, $PO4_2$, $SO4_2$) to the target. Transferring cationic nutrients (NH^{4+}, K^+, Ca^{2+}, Mg^{2+}) requires no surface alteration. The addition of surfactants to the zeolite surface will aid in improving the adsorption capacity [6].

NPs possess superior qualities like higher surface tension, increased surface area, sorption abilities, and highly controlled releasing capacity, making them “a smart delivery system” [7] for the effective distribution of fertilizers to the target areas without much wastage of the payload for a longer duration. Entry of NPs into plants occurs *via* different routes such as cell wall pores, endocytosis, active transport, ion channels, stomata orifices, or root hairs. Entry through the cell wall occurs only if the NP size is smaller than the plant wall pore size (5-20 nm). Engineered NPs with the capacity to induce new pores or facilitate the enlargement of pores are also used to increase uptake efficiency. Near the root system, the outer wall polymer of the nanocapsule is broken down by the organic acids released by the plant, and the nutrients are absorbed eventually [4]. Recently a hybrid NF was created using urea-modified hydroxyapatite (rich in Nitrogen, Phosphorus and Calcium) to which NPs of micronutrients were incorporated. Apart from serving as a single rich source of macro and micronutrients, it also exhibited slow release of PO_4^{3-}, Ca^{2+}, NO_3^-, Zn^{2+}, Cu^{2+}, and Fe^{2+} nutrients resulting in better nutrient uptake and yield in Bhendi plants [8].

Delivery of Nano Fertilizers

NF's delivery methods are designed to ensure that nutrients are delivered efficiently and without waste. Traditional fertilizer application methods cannot provide continuous supply over long periods of time due to NP encapsulation/adsorption. This system has the advantage of minimising fertiliser application frequency, which lessens negative environmental consequences like eutrophication. Modified nanocomposites containing polymers such as hydrogel, sodium alginate, and acrylamide along with clay minerals were used for the

CHAPTER 9

Recent Developments of Graphene-Based Nanotechnology towards Energy and Environment

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Abstract: In recent decades, graphene nanotechnology has emerged as an escalating field of research owing to the excellent physicochemical properties of graphene. Graphene, a single layer of carbon atoms arranged in a honeycomb-like structure, has shown potential utility in multifarious sectors of science and technology such as energy, biomedical engineering, wastewater treatment, environmental pollution, *etc.* Graphene and its composites have been extensively used as electrode materials in energy storage devices such as Lithium-ion, sodium-ion, and metal-air batteries. In addition, graphene-based materials have emerged as potential electrodes material for fuel cells, thereby contributing to a low-carbon economy. Graphene gave a new dimension to electronic industries by replacing the conventionally used material *i.e.*, Silicon (Si) in electronic devices. Moreover, the tunable surface area, functionalization, hydrophilicity, and strong π- π interaction properties of graphene prove its potential applications in medical and environmental science and technology. Recently, graphene-based adsorbents, membranes, and catalysts provide a simple, low-cost, and efficient water and wastewater treatment method. The materials not only detect but also remove various pollutants from wastewater even at very low concentrations. However, due to its extremely small size in devices and components, it is difficult to handle graphene in real applications. Graphene nanotechnology enables the researcher to unfold new properties and functions of graphene in the nanoscale realm providing solutions to unresolved issues related to the health care systems, energy demand, and environmental pollution. These materials not only enhance efficiency but also cause a paradigm shift in many applications. This book chapter sheds light on the earlier investigations, current progress, and future perspective of graphene-based nanotechnology.

Keywords: Air pollution, Energy, Graphene, Nanotechnology, Water treatment.

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Kaushik Pal & Nidhi Asthana (Eds.)

INTRODUCTION

Graphene nanotechnology is an inimitable combination of material and technology which revolutionized the field of scientific study and technological application of the 21st century [1, 2]. Nanotechnology is tailoring any material at an atomic or molecular level in scale from 1 nm to 100 nm for its real-world application. On the other hand, graphene, the unique nanomaterial, has drawn the research attention of every field of science just after its discovery due to its excellent physical, chemical, optical, and mechanical properties [3]. The lightweight and extremely thin properties of graphene make it available everywhere, from human cells to industry [4 - 8]. For example: in the last decade, graphene-based nanomaterials have been employed in biomedical applications like drug delivery, tissue engineering, diagnosis, and biomedicine, *etc.* due to their non-toxicity and biocompatibility [5]. Owing to its abundant oxygen-containing functional group, the graphene surface can easily be modified with targeted molecules, thereby facilitating drug delivery and bioimaging. Moreover, graphene-based nano-electronic, optoelectronic, sensors, and energy storage devices brought a new era in the electronic and batteries industries [9]. Graphene-based LED bulbs, batteries, sensors, and wearable electronics have demonstrated the diverse applications of graphene in the electronic spectrum. Graphene nanotechnology has extended our ability to resolve many critical issues related to energy, environment, and the health care system; the problems which need immediate attention [4, 10]. Specifically, the use of graphene nanotechnology in the energy sector is a two-bird-in-one stone approach, as it fulfills the energy demand and simultaneously protects the environment. This book chapter focuses on the recent breakthrough in renewable energy systems and environmental pollution by graphene nanotechnology from the year 2017 to 2020.

GRAPHENE

Graphene has been termed as a wonder material by many owing to its unique properties such as unparalleled conductivity, extraordinary mechanical strength, flexibility, and transparent nature. In the year 2004, Geim, Novoselov, and the group successfully isolated a monolayer of graphene from 3D graphite by tape stripping method [3]. Graphene is a single atomic plane of sp^2 hybridized carbon atoms arranged in a hexagonal pattern (Fig. **1A**). Moreover, different allotropes of carbon such as fullerenes (0D), nanotube (1D), and graphite (3D) can be obtained by simply rolling, wrapping, and staggering single graphene sheets. The number of graphene layers stacked in the structure regulates the physical, chemical, and electronic properties of graphene. For instance, the surface area of a single layer of graphene is much higher than graphene oxide, few layer graphene, and other derivatives of the same [4]. These exceptional properties of graphene make it a potential candidate for many modern technological applications. The graphene family encompasses graphene oxide (GO), reduced graphene oxide (rGO), and doped graphene.

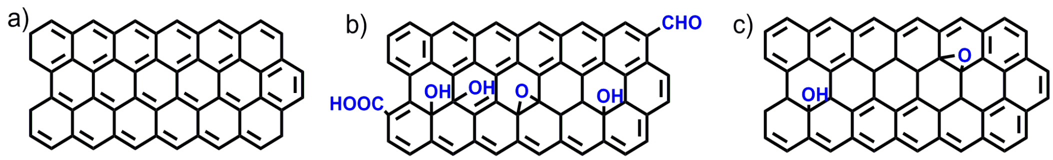

Fig. (1). Structure of **A)** Graphene, **B)** Graphene Oxide, **C)** Reduced Graphene Oxide.

Family of Graphene

Graphene Oxide (GO)

GO is one or a few layers of graphene functionalized with oxygen-containing functional groups (Fig. **1B**). The various oxygenated functional groups on the basal plane of GO enable easy separation of layers and increase the hydrophilicity. It is significant to mention that graphite oxide and GO are two different materials; graphite oxide is a multilayer system with an interlayer distance of 6.35 Å whereas GO consists of one few-layered system.

Reduced Graphene Oxide (rGO)

The electronic, chemical, and mechanical properties of GO can be further enhanced by removing the functional groups from its surface and this reduced form of GO is known as rGO (Fig. **1C**). However, these oxygenated function groups act as adsorption and anchoring sites for the fabrication of composite materials. The removal of oxygenated functional groups from the GO surface opens the possibility to synthesize pristine graphene. However, the complete removal of functional groups is not possible.

Doped GO

The outstanding properties of graphene can be further enhanced by the method of doping. Doping intrinsically altered the electronic structure of graphene thereby, enhancing its electrochemical performance [11]. Substitutional doping is the most stable method of doping owing to the covalent bond between the dopant and carbon atom.

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