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Chemistry, Structures and Advanced Applications of Nanocomposites from Bio-Renewable Resources

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ABSTRACT

Researchers have recently focused on the advancement of new materials from bio-renewable and sustainable sources because of the great concerns about environmental, waste accumulation and destruction, and the inevitable depletion of fossil resources. The bio-renewable-based materials have been extensively used as a matrix or reinforcement in many applications. In the development of innovative methods and materials, composites offer important advantages because of their excellent properties such as ease of fabrication, higher mechanical properties, high thermal stability, and many more. Especially, the nanocomposites (obtained by using bio-renewable sources) have significant advantages when compared to conventional composites. The nanocomposites have been utilized in many applications ranging from food, biomedical, electroanalysis, energy storage, wastewater treatment, automotive etc. This comprehensive review provides chemistry, structures, advanced applications and recent developments about nanocomposites obtained from bio-renewable sources.

Keywords: Bio-renewable sources; nanocomposites; natural polymers; reinforcement; advanced applications

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1. INTRODUCTION

Composites, which are one of the most important materials of modern technology, consist of at least two components comprising a continuous matrix phase and an uncontinuous reinforcement material to obtain the best features from each component. [1] Composites are generally divided into three basic classes according to the size of the reinforcement in the structures. These are macro composites, micro composites, and nanocomposites. Nanocomposites that provide quite outstanding features can be prepared by the application of reinforcement (below 100 nm in size) phase in the composite. [2,3] Because of the high surface-to-volume ratio of nanocomposites, interaction between matrix and reinforcement is very high. Despite having a very short history, nanocomposites have been frequently used in many applications due to their superior properties. Applications of nanocomposites have been considerably developed in engineering, plastic, rubber, coating, adhesive, electronic and optic materials. [4] However, this rapid growth has also brought some problems and created severe environmental problems due to the late decomposition periods of nanocomposites in nature. The most important solution to eliminate these problems is the preparation of nanocomposite components from bio-renewable resources. For this purpose, nanocomposites are obtained from bio-renewable resources by the use of vegetable oils, cellulose, starch (S), lignin, chitin, natural rubber, and proteins to name a few. These nanocomposites are mainly divided into three groups in terms of structural type. These reinforcements are composites obtained from bio-renewable sources, composites that their matrix is originated from bio-renewable sources, and composites that have both reinforcement and matrix component obtained from bio-renewable sources.

The most important common features expected in nanocomposites made from bio-renewable resources are biocompatibility, biodegradability, easy preparation, low density, inexpensive and suitability for modifications.[5] Besides these commonly seen features, low thermal conductivity, increased flexibility, low dielectric constant, good workability depending on the application are also general properties of these structures.[6,7] However, the lower thermal, mechanical and chemical stability compared to petroleum originating structures has restricted their industrial applicability in many applications. To improve these properties, many studies are being carried out in this area.

Nanocomposites made from bio-renewable resources reveal a greener approach than petroleum-derived composites and they are used especially in food, packaging and biomedical industries. Besides, these nanocomposites exhibit high potential to have applications in several areas such as membrane, sensor, energy storage, optic, automotive and flame retardant (Figure 1).

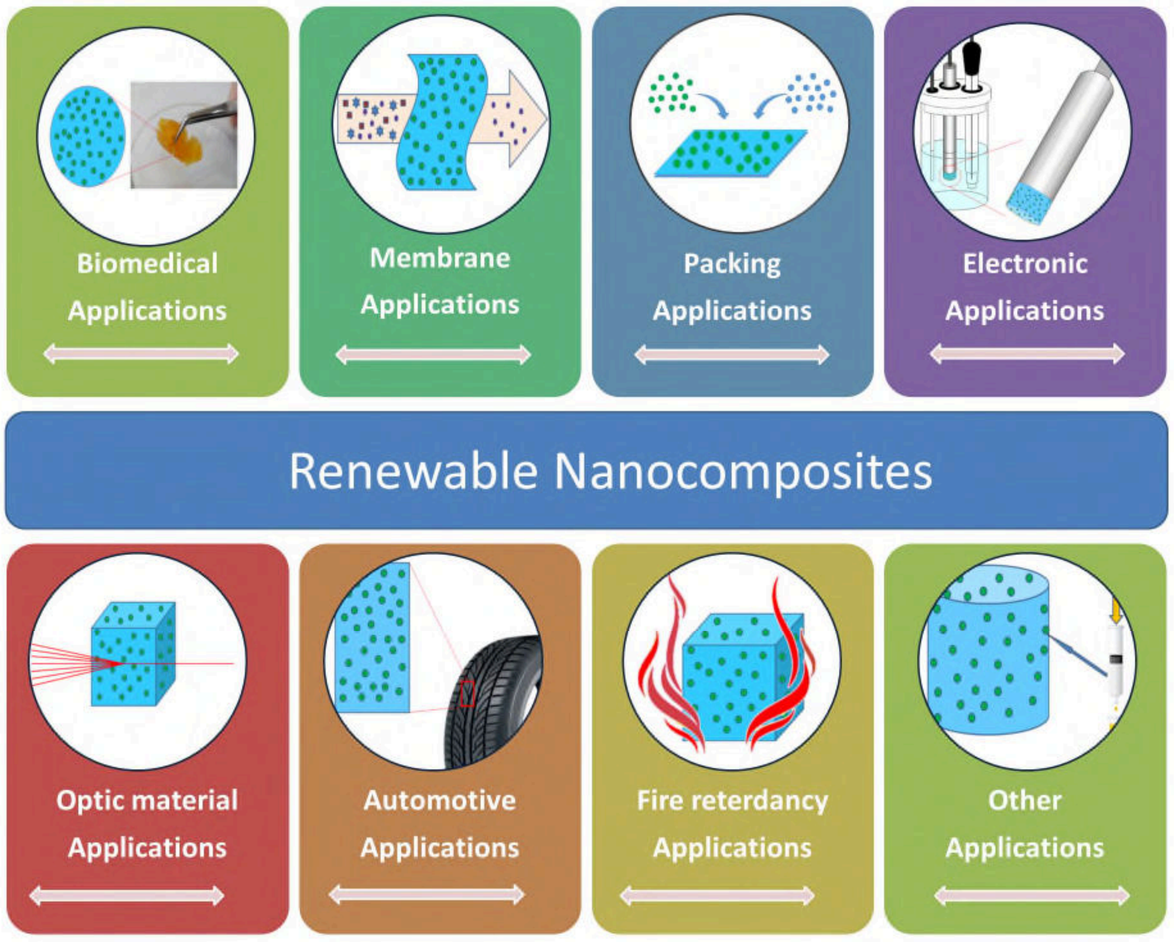


Figure 1. Application areas of nanocomposites obtained from bio-renewable resources.

This review consists of a detailed discussion of chemistry, structure, advantage and disadvantage of the applications of nanocomposites made from bio-renewable resources in the aforementioned areas. Besides, this review aims to provide information on recent developments in polymer nanocomposites containing bio-renewable nanomaterials with special attention to several promising applications.

1.1. Overview of Nanocomposite Materials Containing Petroleum-Based Polymers

Nowadays, petroleum-based polymers are present almost everywhere in our daily life. Polypropylene, polyethylene, nylon, polytetrafluoroethylene, and polyester are the most common examples of synthetic polymers. These polymers have originated from petroleum hydrocarbons. [8] In our daily life, synthetic polymers are used since most of them have versatile characteristics such as chemical inertness, resistivity, strength, and flexibility.[9–11] For instance, related to their high tensile strength, petroleum-based polymers have such a variety of applications from tires to sails. When petroleum-based polymers are used as a woven material, it is especially beneficial for underwater applications. [12] Unfortunately, lots of important problems have been associated with the usage of synthetic polymers. [12,13] Most desirable features of many synthetic polymers have many advantages such as inertness, resistance against chemical and biological degradations. However, these features also mean that they will last a long time after being discarded. For instance, researchers have reported that five hundred years are needed to disintegrate a plastic bag. [14]

Until the recent past, synthetic polymers have been widely used for manufacturing of composites. [15] However, the usage of these polymers exhibits huge challenges and problems. [13,16] These challenges include a scarcity of organic reagents because of decreasing oil and gas sources year by year and at the same time rising in oil and gas prices. Other disadvantages of using synthetic polymers have environmental issues related to their incineration, global warming effects, and cross-contaminations as well as toxicity risks for consumers. [12,17,18] These concerns have brought solutions for the new generation materials that can defeat these handicaps and proceed with the desired features for different applications. Thus, to diminish the extensive usage of petroleum-based polymers, researchers have been investigating the design of polymer composites in terms of better performance and cost. Moreover, graphite, glass fibres, clays silica, carbon nanotubes, and silica have been often used as reinforcement materials during the production of these polymer composites. [9] However, these reinforcements are generally non-degradable, inorganic and occasionally petroleum-based materials. Thus, engineers and researchers are still trying to easily produce nanocomposites that are made of natural, bio-renewable and completely biodegradable resources. Some researchers have reported that bio/natural fibres reinforced polymer exhibit a positive effect on the advancement of product characteristics. [8,10] Bio-renewable nanocomposites have been extensively researched since there are urgent needs to develop biodegradable polymers, extinguishing in the usage of fossil-based raw materials, and decreasing of CO_2 release. The use of agricultural sources for the preparation of nanocomposites from bio-renewable resources is one of the reasons why bio-renewable nanocomposites have been getting attention for researches recently. The utilization of these nanocomposites is hoped to elevate the speed of manufacturing and recycling with increased environmental friendliness. The significance of the bio-renewable nanocomposites in different industries has become very imperative because of their desired mechanical, flame retardancy, resistance, electronic, and thermal isolation characteristics. [19,20]

1.2. Need for Nanocomposites from Bio-Renewable Resources

In recent years, serious problems related to petroleum-based polymers have arisen. These petroleum-based polymers cause the gigantic amount of wastes that are stockpiled on our earth facing with huge negative environmental impacts and extremely high recycling costs. [21,22] Soon, especially in 2050, it is anticipated that the magnitude of petroleum-based polymer wastes will be grown by at least three-fold, unfortunately. [23] Even though petroleum-based polymers have lots of negative impacts on the environment, they have a constructive and synergic blend of structural features such as flexibility, thermal performance, transparency and strength. Until now, petroleum-based polymers have become the most chosen polymers for many industrial applications because of their excellent chemical and physical properties. Nevertheless, according to the plastics recycling and recovering data results, post-consumer plastic waste that can be reused is estimated to be only 39.5%. [24] The remains have harmful effects on soil, water, and air, so, it affects wildlife, habitat and also human health. Therefore, we also face an increased risk of falling victim to illness and disease. To minimize the negative environmental effects of post-consumer petroleum-based waste, bio-renewable and eco-friendly materials are the most suitable resolutions. [25,26]

Natural polymers offer attractive advantages such as biodegradability (by an enzymatic or hydrolytic mechanism), renewability, biocompatibility, non-toxicity, eco-friendly and low cost. Additionally, they can be easily functionalized according to their application potentials. However, low mechanical properties and little water resistance are the main disadvantages of the materials, thereby, their use is heavily limited. To eliminate the natural material's disadvantages, nanocomposites from bio-renewable resources have been produced via various techniques to enhance the mechanical features (tensile, flexural and impact). So far, bio-renewable sources such as chitosan (CH), cellulose, β-Cyclodextrin (β-CD), alginate have been extensively utilized as a matrix or fillers to fabricate Bio-Nano composites. In today’s world, nanocomposites from bio-renewable resources have a wide role and will play an increasing role in numerous industrial applications. These applications include drug delivery, tissue engineering, fuel cells, electronics, food packaging, environmental remediation, genetic engineering, and biomedical sciences. [27]

1.3. Bio-Renewable Resources Used for Nanocomposites Preparation

Bio-renewable nanocomposites can generally be evaluated in three groups. These are nanocomposites containing renewable additives, nanocomposites containing bio-renewable resource matrix and nanocomposites having both additive and matrix structure based on bio-renewable resources. Examples of such bio-renewable materials include cellulose, starch, chitin, chitosan, pectin, hyaluronic acid, lignin, terpenes, vegetable oils, proteins (keratin, silk, gelatin, gluten, albumin, etc.) and natural rubber.[28-15]

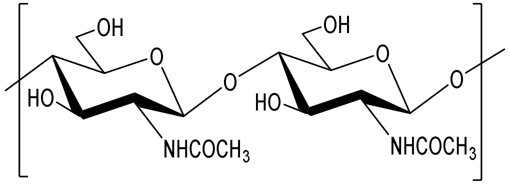
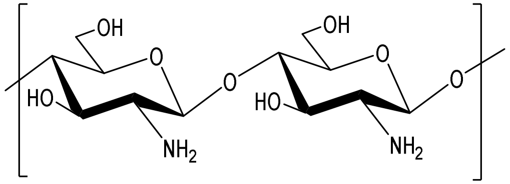
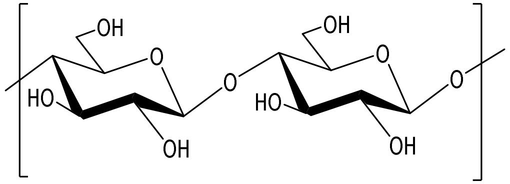
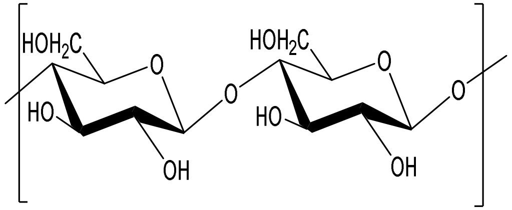
Starch and cellulose have an important place as a plant-based additive and matrix material. It is the most widely used biopolymer especially in the field of starch composite.[29–32] It is generally employed as a matrix because of its ease of availability, low cost, the advantage of biodegradability and ease of processing. These are used to increase biocompatibility in medical applications and to increase the adherence of active substances to the composite structure. Mixtures with more than 85% starch can be used in injection moulding and foam manufacturing.[33] Starch-based composites and starch structure have deprived physical properties for example high hydrophilicity, high biodegradability, low thermal strength, and low decomposition temperature.[34] Therefore, in the manufacturing of starch-based composites, modification of the starch structure may sometimes be required. The cellulose structure is generally preferred for imparting mechanical strength to the nanocomposite structure as a natural fibre. [35] Cellulose is one of the most natural polymeric structure found in the environment. It is generally used in wood structures, as cellulose fibres, as microcrystalline cellulose or as hemicellulose, and as cellulose nanocrystals extracted from bacteria, tunicate and algae, etc. in composite structures.[35] Cellulose improves biocompatibility and biodegradability as well as increases mechanical properties as additives.

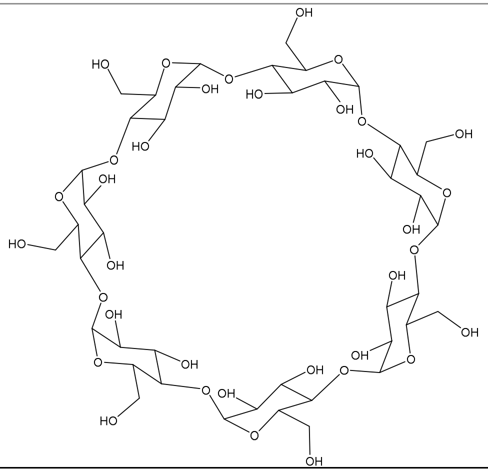
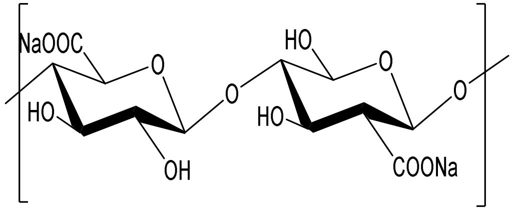
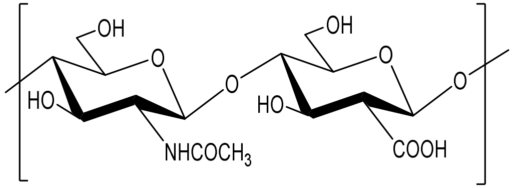
Chitosan is a widely available linear amino polysaccharide in nature and has been used in the production of many different composites.[36,37] It is insoluble in organic solvents, alkali, and water.[29] However, it is soluble in some diluted inorganic/ organic solutions and has antimicrobial properties, high absorption ability, radiation stability, bioinert and biocompatibility. Because of these properties, water treatment, drug release, food packaging, synthesis of biocompatible structures is very important in applications. Due to these common properties, it is very popular in composite chemistry. Chitin is a non-toxic, physiologically inert, biodegradable polysaccharide with high mechanical stability and strength.[38] After cellulose, it is one of the most common natural polysaccharides.[39] Therefore, chitin has been frequently used in polymer composite structures to enhance the mechanical properties of materials.

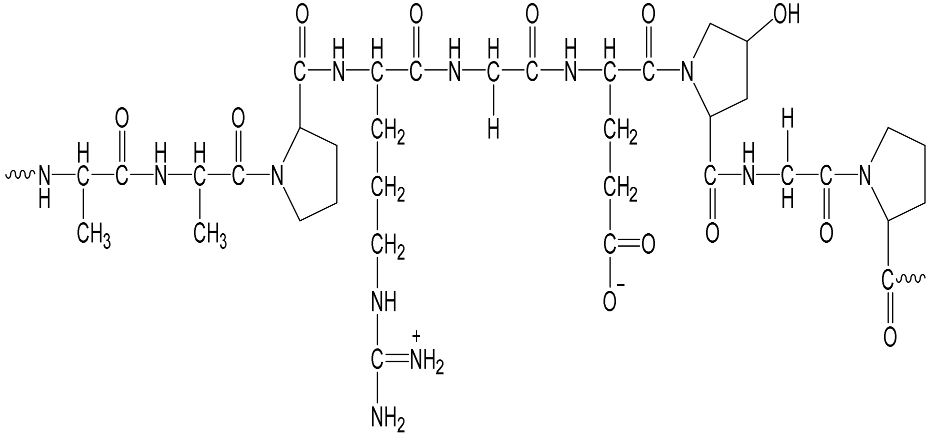
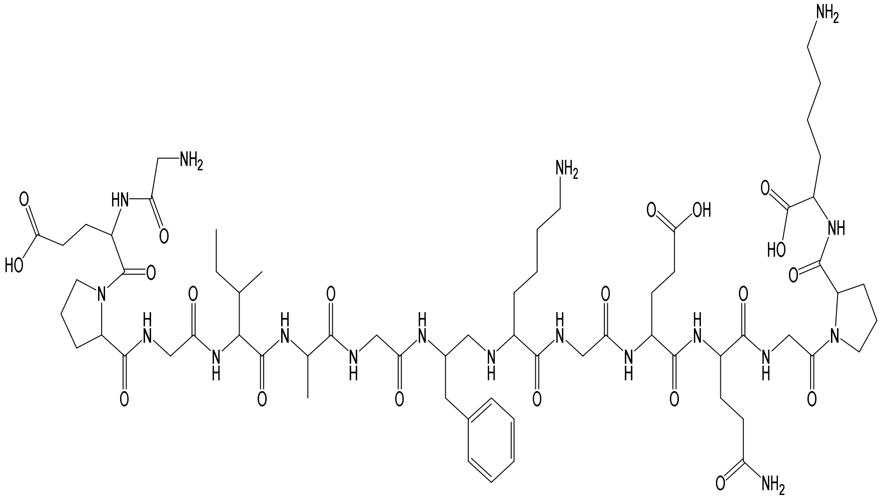
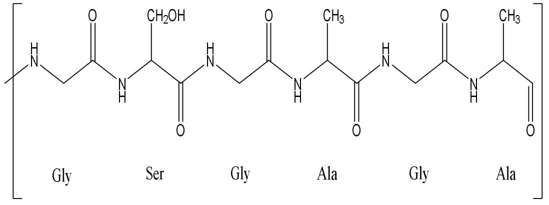
Another important edible source used in composite structures is vegetable oils.[29] This source, which is quite cheap and widely used, is employed in composite structures in two ways. The first method is the synthesis of polymers and composites of unsaturated oils through double bonds. The second method is the preparation of polymers and composites by obtaining fatty acids. The unsaturation levels of fats are important in both methods. Polymer syntheses can be made directly via double bonds in oil or polymeric structures can be made by modifications such as epoxidation and acrylation. Today, polyester, polyurethane, polyolefin copolymers or polymeric resins have been successfully synthesized from vegetable oils. Composites of these synthesized polymers can be widely seen in many applications.

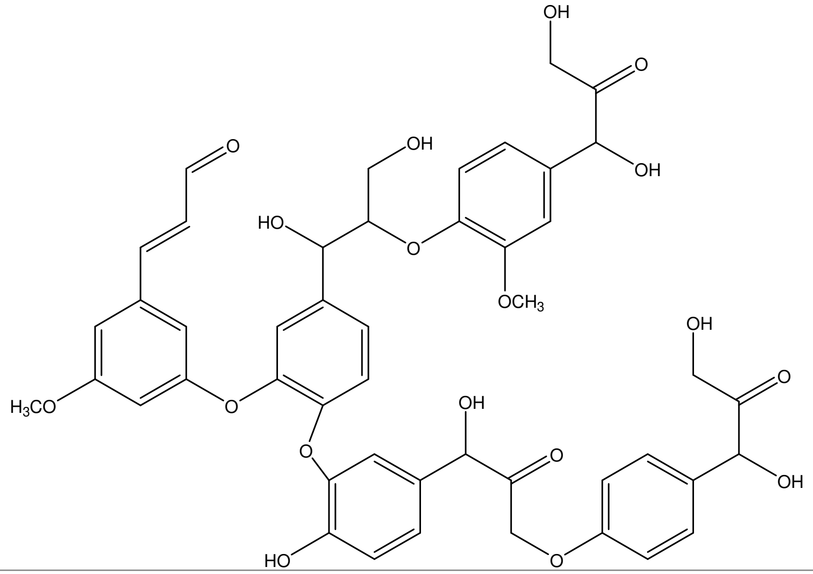
Detailed bio-renewable resources used in the nanocomposites are also given in Table 1 with chemical structures, advantages, and disadvantages.

Table 1. Summary of chemical structures, advantages, and disadvantages of various bio-renewable resources

Natural scaffolds	Chemical Structure	Advantages	Disadvantages
Chitin		Nontoxic, biodegradability, abundance and renewability	Low mechanical resistance
Chitosan		Natural cationic copolymer, excellent biocompatibility, low toxicity, biodegradability, and broad-spectrum antibacterial activity[40]	Low mechanical resistance, low porosity
Cellulose		Biocompatibility, derivatizability, low density, nonabrasive, combustible, non-toxic, low cost, and biodegradable, renewability[41]	Poor interfacial adhesion, low melting point, and water sensitivity
Starch		Nontoxic, biodegradability, abundance and renewability	Ageing, and poor mechanical performance

β-Cyclodextrin		High water solubility, low viscosity, low toxicity, and low immunogenicity	Poor mechanical performance
Alginate		Biocompatible, easily functionalized, good cell recognition biocompatible, simple gelation methods	Poor mechanical performance
Hyaluronic Acid		Consistency, biocompatibility, hydrophilicity, unique viscoelasticity and limited immunogenicity[42]	Rare allergic reactions

Gelatin		Natural origin, low cost vascular, good mechanical property, excellent oxygen barrier property	Solubility
Collagen		Biodegradable, non-antigenic, non-toxic and biocompatible, easily modifiable, ready availability and easily purified from living organisms[43]	High cost, side effects, complex handling properties, rapid release, the inconsistency of isolated collagen[43]
Silk fibroin		Natural protein, tunable biodegradation rate, non-immunogenic, biocompatible, good transparency, good mechanical strength[44]	High cost, lack of data about clinical efficacy [44]

Lignin		Inexpensive and renewable High carbon content Already oxidized[45]	The complex and disordered structure Diversity May crosslink during melt-spinning[45]

1.4. Processing Methods of Nanocomposites from Bio-renewable Resources

Nanocomposites from bio-renewable resources can be produced easily by those methods through which common composites are produced in general. These methods are melt mixing, in-situ polymerization, solution mixing, melt inter-chelation, precipitation, extrusion, sol-gel process and spray mixing, etc.[3] Besides, layered composite structures can be synthesized by hand-lay-up and spray-lay-up technique using natural fibres. Also, many new methods such as electrospinning, nanofibre direct dispersion techniques are successfully being used in the preparation of nanocomposites from renewable sources. However, some of these methods remain at the level of academic study only and are not used in industrial production. In the industrial production dimension, generally simpler and less processing steps are preferred. Before all these techniques, the use of renewable resources is realized by two methods. Sustainable polymers and composites from bio-renewable sources may be produced by certain modifications of chitosan, starch, cellulose gluten, or gelatin.[46,47] In this way, the basic properties of natural polymers such as biocompatibility, biodegradability, easy processability are transferred to the obtained composites. Biologically based polymers from renewable sources have been also produced from biomass or agricultural wastes in a two-step process [47–49], which are abundant. In particular, techniques such as melt intercalation, extrusion, and in-situ polymerization which are commonly applied to the production of polymeric nanocomposites, have been applied to bio-based polymeric composites in the last decade.

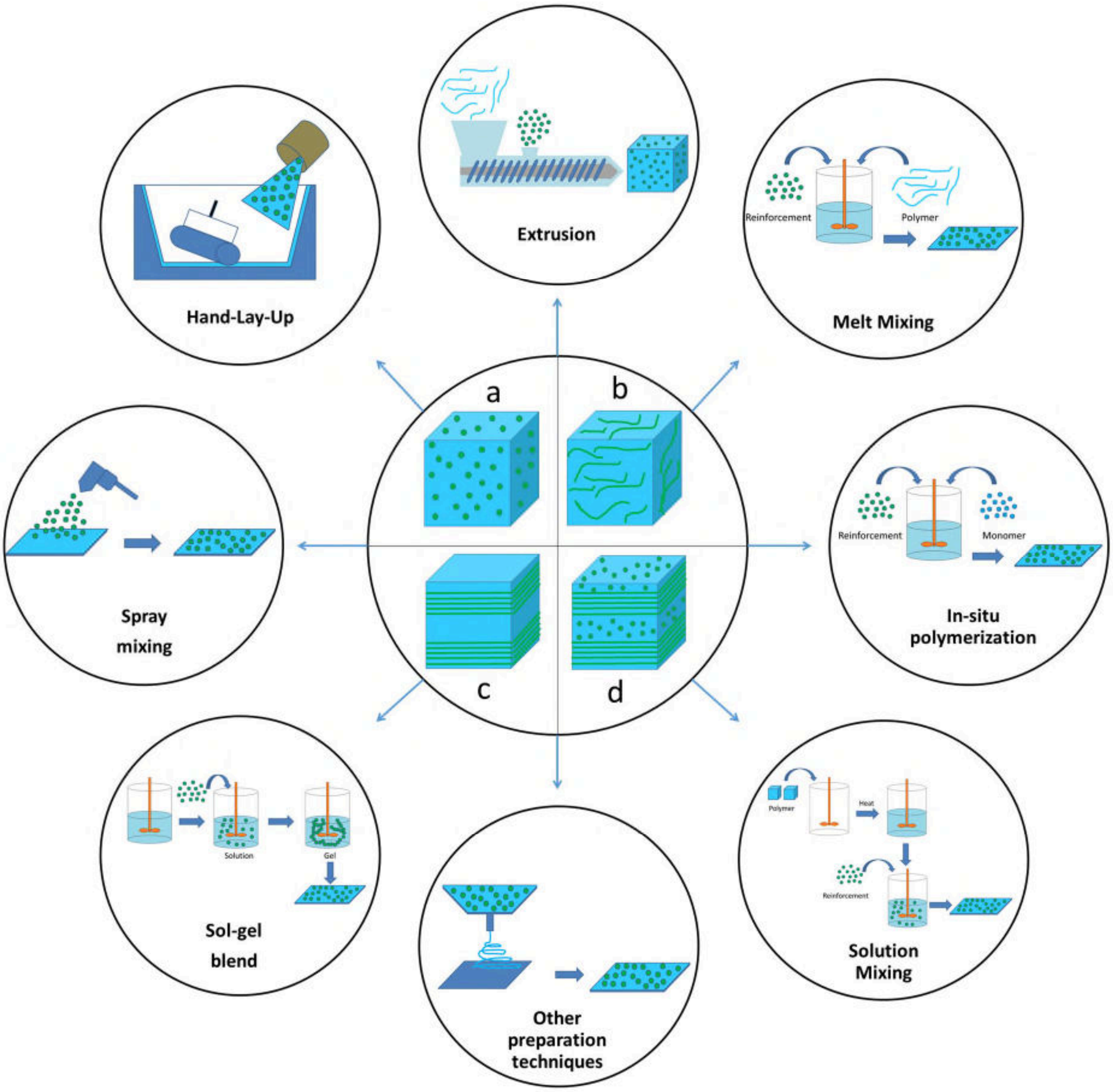


Figure 2. Preparation methods of nanocomposites from bio-renewable (A, B, C, and D are the types of bio-renewable composites).

1.4.1. Melt mixing

This technique is widely used for the preparation of composite .[50] In this technique, the matrix material is first made liquid by heating above the melting point. The composite is moulded or shaped by controlling the additive into this liquid melt. In this process, fusible structures, such as gelatin, which are generally isolated from renewable sources, are used as the matrix, while most renewable sources can be used as additives. Structurally renewable fibre is a more appropriate technique for the production of particulate or layered additive composites.

1.4.2. *In-situ* polymerization

It is a technique performed mainly by polymerization of the monomer structure containing the additive.[50] At the time of polymerization, since the additive is present, the additive would be dispersed into the matrix. In this method, cellulose, chitin, starch, lignin, which are renewable additives, can be converted to composites during polymerization of commonly used organic monomers. Another renewable source-based composite synthesis in this technique is the polymerization of monomers obtained from renewable sources. Particularly during the polymerization of terpenes and terpenoids, nanocomposites can be synthesized by the addition of nanostructures such as clay, CNT and graphene. Another example is the conversion of double-bonded or epoxidized monomers from vegetable oils into nanocomposites with common additives. In composite production with the in-situ polymerization technique, additive agglomeration remains at a minimum level. Therefore, the homogeneity of the produced materials is quite high.

1.4.3. Solution mixing

This technique is generally preferred for academic studies. In general, the matrix material is dissolved with a solvent and mixed with the additive. Then the composite structure is obtained by coating, moulding or film casting techniques. The amount of the solvent used, its toxicity, and the removal of the solvent after composite formation are some of the disadvantages of this method.

1.4.4. Extrusion

Extrusion is the economically most important and most preferred production method for thermoplastic-based composites and nanocomposites. Extrusion allows the raw material to be melted and pushed through the melting channel having single or multiple screws to take the shape in the outlet block. During this process, nanocomposites can be readily prepared by incorporating nanoscale additives into the molten raw material. Some natural fibre reinforced PP composites had been prepared with an injection moulding process.[51] Unsaturated polyester, epoxy, and vinyl ester resins were then used extensively in the preparation of such composites. Due to its suitability for mass production and practicality, the most common and important production technique is the extrusion and injection moulding techniques. However, the technique is only suitable for the production of thermoplastic composites. This increased production has led to the emergence of many technological products. Also, this increased production enables the application of new production methods.

1.4.5. Sol-gel process

The sol-gel technique is based on the hydrolysis of a metal alkoxide and subsequent hydrolysis.[52] In this technique, metal oxide nanoparticles such as SiO_2, TiO_2, ZnO can be prepared or prepared in ceramic matrices. Therefore, it is a frequently preferred technique for the preparation of inorganic metal oxide additives in the process of manufacturing nanocomposites from renewable sources. However, metal requires expensive chemicals such as alkoxides that are moisture-resistant and expensive.

Sol-gel methodology and hybrid composite production techniques, which are used to overcome the mechanical strength problem, which is a fundamental problem in bio-based composites, are still at the academic level and are not frequently applied industrially. In particular, an adaptive molecule is bonded to the surface of the matrix to increase the mechanical properties and to eliminate the phase difference between the additive and the matrix material. The bonding technique with a strong covalent bond to the matrix structure is very promising for the future.

1.4.6. Hand-Lay-Up and Spray-Up techniques

In addition to the above mentioned innovative methods for the preparation of composites from renewable sources, traditional methods, for example, hand-lay-up and spray-up are also used.

The simplest production technique is hand lay-up technique to produce bio-based composites from renewable sources. In this method, composites containing up to 30% of additives can be produced. In this technique, bio-based additives are introduced into the preformed mould and matrix resin is applied to the fibre with simple hand tools such as a brush. In the hand-lay-up method, the fibre or fibre-structured additive is deposited on a mould and impregnated with liquid resin.[24-53] This process is continued until the desired thickness of the material is obtained. In particular, this technique is frequently used in polyester, epoxy resins, vinyl ester, and phenolic resins. The hand-lay-up method is commonly preferred for a small number of productions. In this technique, resins obtained from renewable sources can be used very easily. There are many examples of composites prepared especially with vegetable oil-based resins. Mixing coating and spray-mixing (Spray-up) techniques are the mechanized forms of hand lay-up and are used to obtain several products. With a spray gun, the mixture of chopped fibres and liquid resin is sprayed onto the open mould to form the mould. In these techniques, natural fibres and resins are generally sprayed simultaneously into or onto the mould. The additive phase in the form of fibres, nanoplate, particles or fabrics is sprayed onto the surface of the container together with the resin mixed with the curing agent with an application-specific spray-gun. After spraying, the surface is dried and the composite structure is obtained.

1.4.7. Resin Transfer Molding or Resin Injection Methods

Resin transfer moulding or resin injection is another common nanocomposite preparation technique. This method uses a two-piece mould, while the manual tilting system makes it faster and has a long service life. Felt, fabric and both of them are used as reinforcing elements. The reinforcing material is first placed in the mould and closed to fill the mould. It is coated with late-resins in the matrix to prevent the fibres from entering into the mould. The resin is pumped into the mould under pressure, but this process is very time-consuming. In this method, it can be vacuumed to evacuate the interior air and to thoroughly penetrate the resin into the fibres.

1.4.8. Other methods

Electrospinning, centrifugal casting, pultrusion or nanofibre direct dispersion techniques are also used to prepare nanocomposites from renewable sources. Electrospinning is generally accepted as a single-stage, simple, reliable, effective and inexpensive technique for producing different synthetic or natural polymer-based nanofibres in diameters ranging from micrometers to nanometers. [54] Electrospinning and polymer-containing nanofibre production is the most advantageous method of nanofibre manufacturing and offers the user a wide range of biomaterial production. The use of nanofibres produced by this method is also quite high. Nanofibrous polymer materials designed with electrospinning have been preferred and have attracted great attention because of their excellent characteristics such as high aspect ratios, surface area-volume, variable pore sizes, and oxygen permeability. These properties make them outstanding candidates for a variety of applications, such as nonwoven mats of electrospun fibres, dressings, and drug delivery systems. In this method, the polymer solution prepared in the desired properties is dissolved in a suitable solvent and placed into the syringe. After this first step, the electrical solution is applied to the plate opposite to the syringe at a high potential ranging from 5 to 50 kV to generate an electrical field. At the end of the syringe needle, due to the surface tension force, the polymer solution appears as a hemispherical shape. At this time, when the potential difference reaches a certain threshold value, the spherical polymer droplet becomes conical and extends and forms fibre. The fibres formed are collected by a conductive collector. With this method, many nanocomposites based on bio-renewable resources have been produced especially as drug delivery systems, wound dressings, or tissue support systems.

2. Chemistry, Structure and Biomedical Applications of Nanocomposites from Bio-Renewable Resources

The first polymeric materials used by mankind are wool, starch and cellulose obtained from nature and protein-derived animal shell & horns. Many of these natural polymeric structures are still used in many industries. These natural sources are chemically structured as polysaccharides, proteins, polyester, and mixed composites. Guar gum, pectin, cellulose, chitin/CH, dextrin and dextran structures are used as polysaccharides. Among protein-based natural polymers, wool, silk, gelatin, collagen, casein, albumin, and fibrinogen are the most preferred structures. Besides, since natural polymers are originated from plants, frequently used natural polymers such as polyhydroxialconates, lignin, natural rubber (polyisoprene) and polyglutamic acid are renewable structures. These polymeric structures are produced in nature by plant or animal origins and the composites prepared by using these polymeric structures are bacterially or hydrolytically biodegradable in soil. The other basic feature of medical materials is biocompatibility; in other words, the desired applications are possible without causing any side effects in the human body. Although bio-based polymers are preferred as biocompatible materials for clinical applications, nanocomposites formed from renewable sources have recently received increased attention. [55] Versatility and easily adaptation to many systems of nanocomposites obtained from bio-renewable resources are the main reasons for this interest over synthetic materials for being utilized in many biomedical applications. Particularly, the four major categories of medical applications for nanocomposites from bio-renewable resources have come to the fore: drug delivery, gene therapy, antimicrobial, and tissue engineering applications (Figure 3).

2.1. Drug Delivery Applications

Drug delivery systems include formulations that have been created for the delivery of pharmacological agents into desired regions more reliably. [56] Being directed for the drug to the target zone is important both for more effective treatment and reducing side effects. Therefore, the creation of drug delivery systems containing different components exhibits intense importance. In this context, especially nanocomposites and their types including bio-renewable components are promising, and many studies are being carried out on drug delivery applications. Drug releasing mechanisms in these studies include different stimulating factors such as temperature, pH, light, etc. (Figure 4).

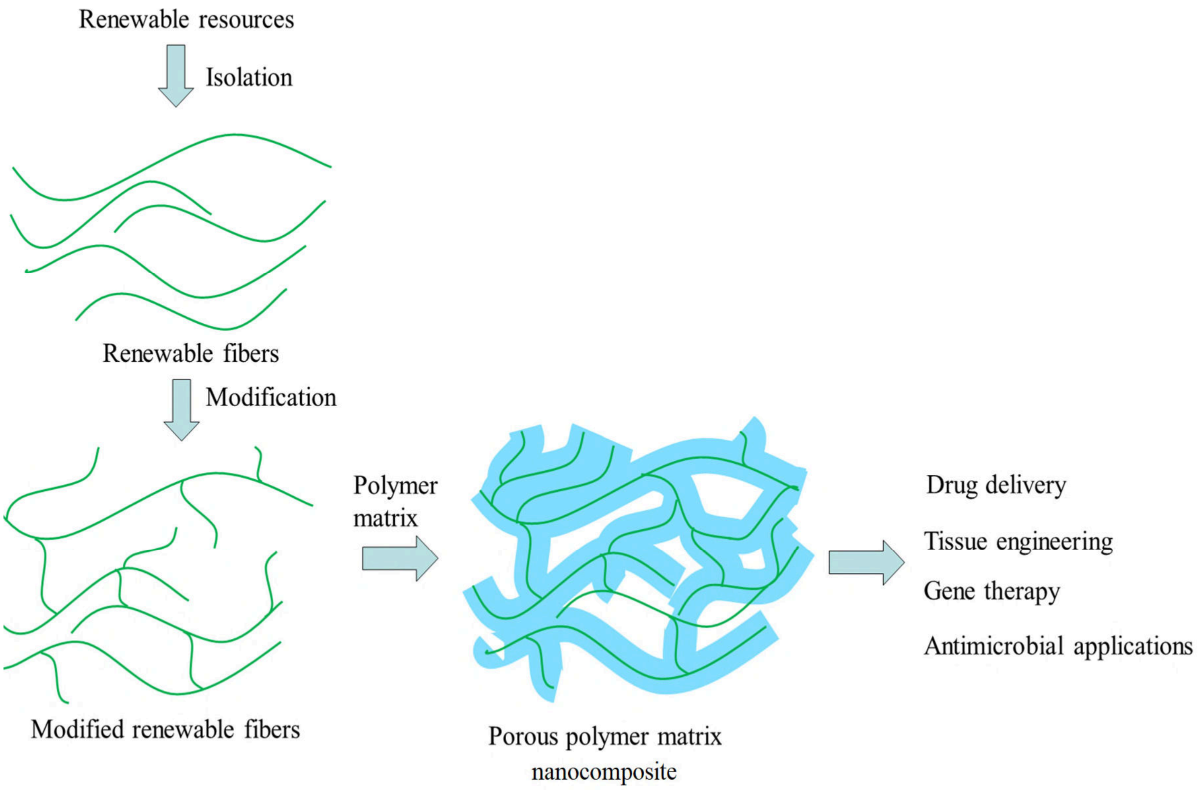


Figure 3. Preparation methods of nanocomposites obtained bio-renewable sources for biomedical applications.

Specifically, the surface of the nanoparticles can be well functionalized with different groups and made suitable to attach the drug molecule (Figure 5). In this way, the release of many drugs in different structures and functions can be performed practically.

For instance, a biological nanocomposite, hydroxyapatite (HA)/collagen alginate had been improved not only as a bone filler but also a drug delivery tool. The nanocomposite was incorporated with the bone formation protein, which is a growth factor. [57] Furthermore, the

HA/collagen scaffolds which have porous structures had also been used for fibroblast growth factor-2. This drug releasing system had given the desired results by inducing the regeneration of cartilage and bone for *in vivo* models. [58] Apart from these, HA/CH nanocomposites had been used as a drug-delivery matrix and a precise release of vitamins had been realized from that matrix. [59]

For the controlled release of drugs, double-layered hydroxide nanocomposites have been presented as another fascinating strategy. In the production of nanocomposite structures, they can serve as hosts for the addition of biopolymers between the double-layered hydroxides. Anionic polysaccharides such as alginate, carrageenan, and pectin have been used to form *N*-hydroxyl layered double-hydroxide matrixes. [60] Moreover, layered materials can also behave like a molecule transfer for biomedical applications. [12]

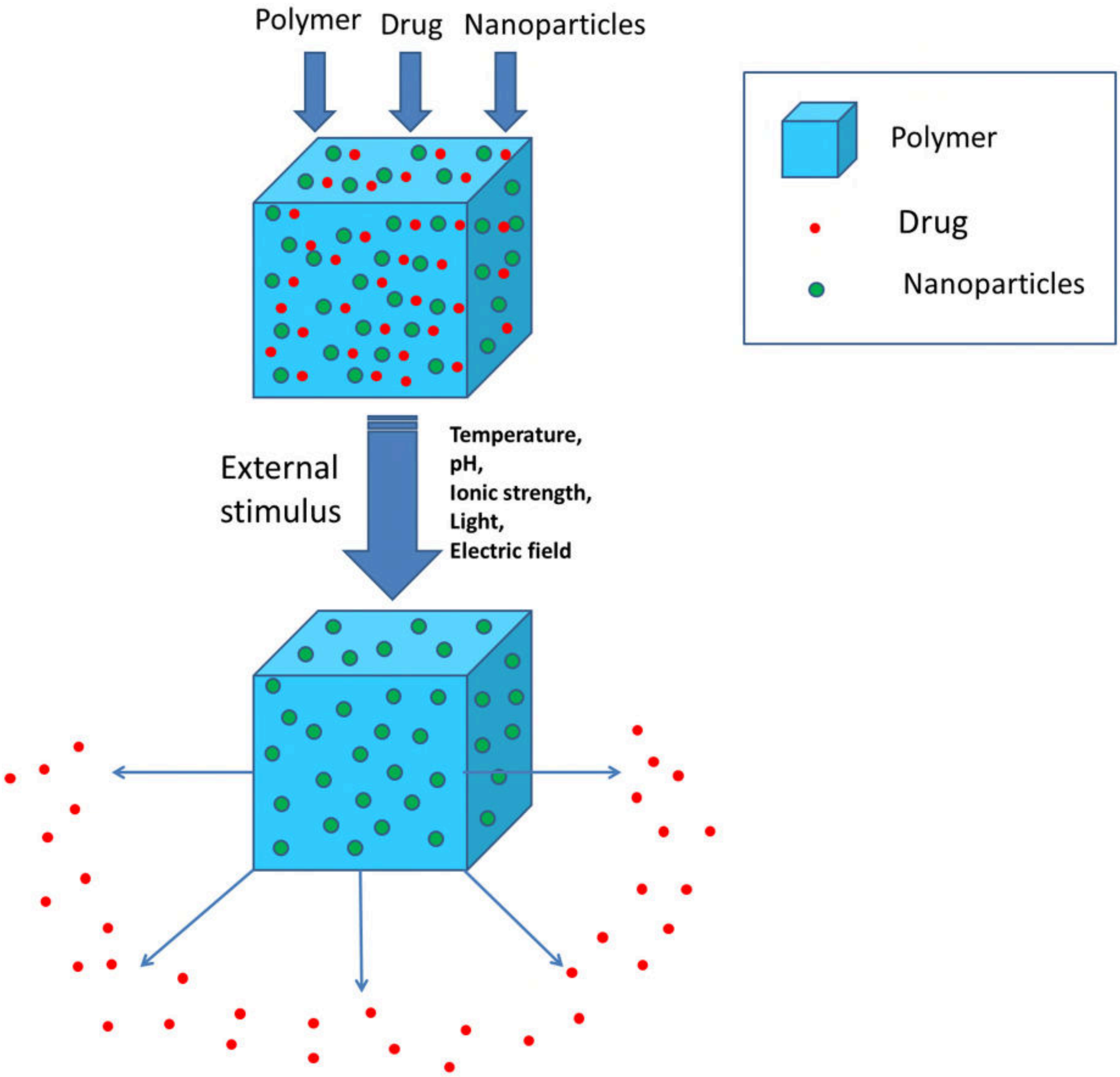


Figure 4. Illustration of nanocomposites for the drug delivery system.

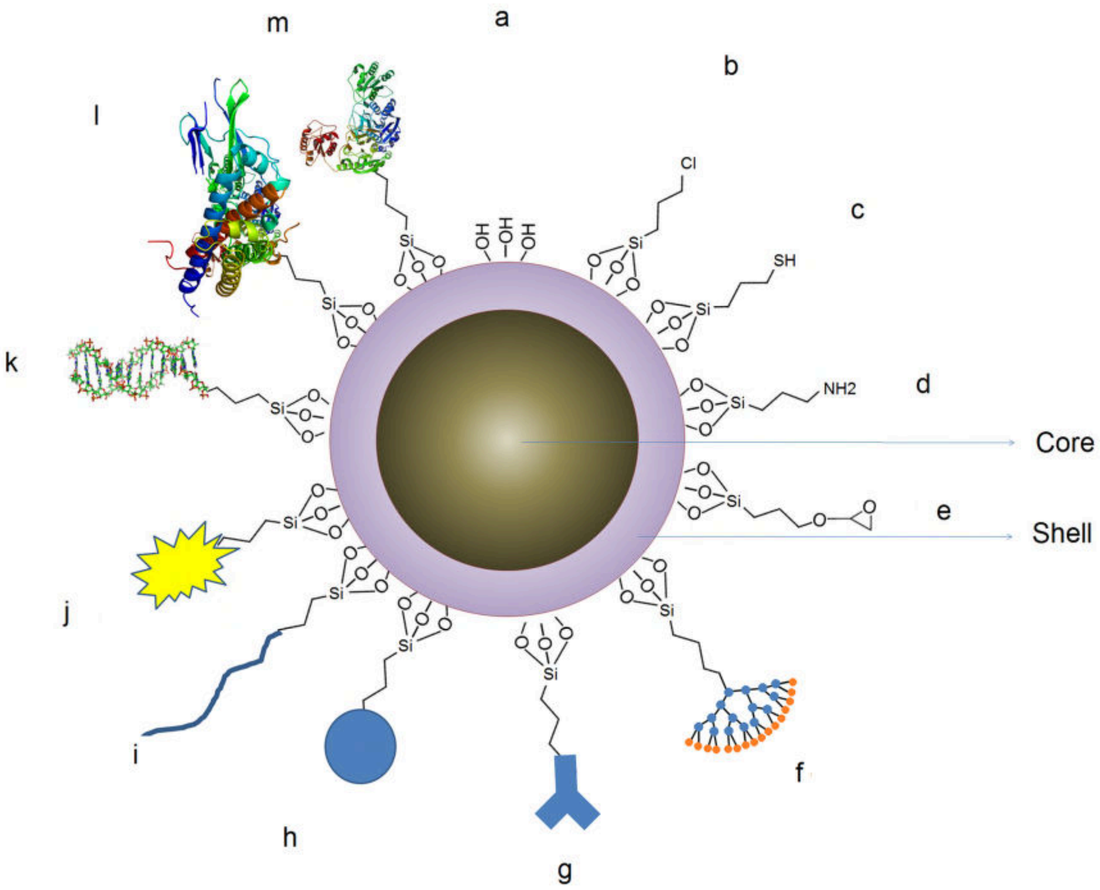


Figure 5. Modification of core-shell nanoparticles. (a; free surface, b; chloro functionalized particles, c; -SH functionalized particles, d; -NH$_2$ functionalized particles, e; epoxide functionalized particles, f; dendrimer containing particles, g; antibody, small organic group or drug functionalized particles, I; polymer bounded particles, j; florescent group containing particles, k; DNA bounded particles, l; protein bounded particles, m; enzyme-containing particles

Layered double-hydroxide polylactic acid composites have been functionalized with ibuprofen, an anti-inflammatory drug. [61] Natural biopolymer xyloglucan which is extracted from Jatoba seeds in Brazil with layered double-hydroxides has been produced as a means for slow release of enalaprilat, an anti-hypertensive agent. [62]

The multifunctional core-shell nanogels have been also prepared by Wu et al. for simultaneous optical temperature and targeted tumor sensing. [63] The targeting ligand was the hyaluronic acid chains. Also, the thermoresponsive nanogels based on polyethylene glycol (PEG) had an Ag-Au bimetallic nanoparticle core used for imaging. To initiate the release of the therapeutic drug depending on the local temperature increase of the targeted area, near-infrared (NIR) irradiation was used. For the encapsulation of different compounds, lignin is also used as nanoparticles since it is cheap, bio-renewable and eco-friendly material. There are lots of pharmaceutical applications in which lignin is commonly utilized. Because of having economic and positive ecological characteristics, lignin is a good candidate for encapsulation of different nanoparticles in a variety of pharmaceutical applications. For instance, using an anti-solvent precipitation method, Frangville et al. have prepared lignin nanoparticles that had sizes ranging from 100 nm to microns. Different production methodologies were used during the synthesis of LNPs (Figure 6). [64,65] Nanoparticles today have significant potential in drug delivery systems. Lignin nanoparticles (LNPs) didn't exhibit any toxicity in terms of cells, especially for yeast and microalgae. So, these LNPs are being utilized as desired tools not only for drug delivery applications but also for cosmetic and pharmaceutical products.

Furthermore, LNPs may be utilized as adsorbents to eliminate environmental contaminants from the contaminated regions. Richter et al. have used a precipitation method to assist the synthesis of LNPs. These LNPs were prepared using Ag^+ and treated with poly diallyl dimethyl ammonium chloride (PDAC) for coating. [66] The coated material was biodegradable and environmentally friendly. So, this coating also helped the adhesion of the LNPs to the bacterial membranes. At the end of this process, it could effectively kill different varieties of bacteria. Fortunately, by producing these metallic silver nanoparticles (AgNPs) having elevated antimicrobial activity as well as biodegradable cores, it is possible to reduce the negative environmental impact.

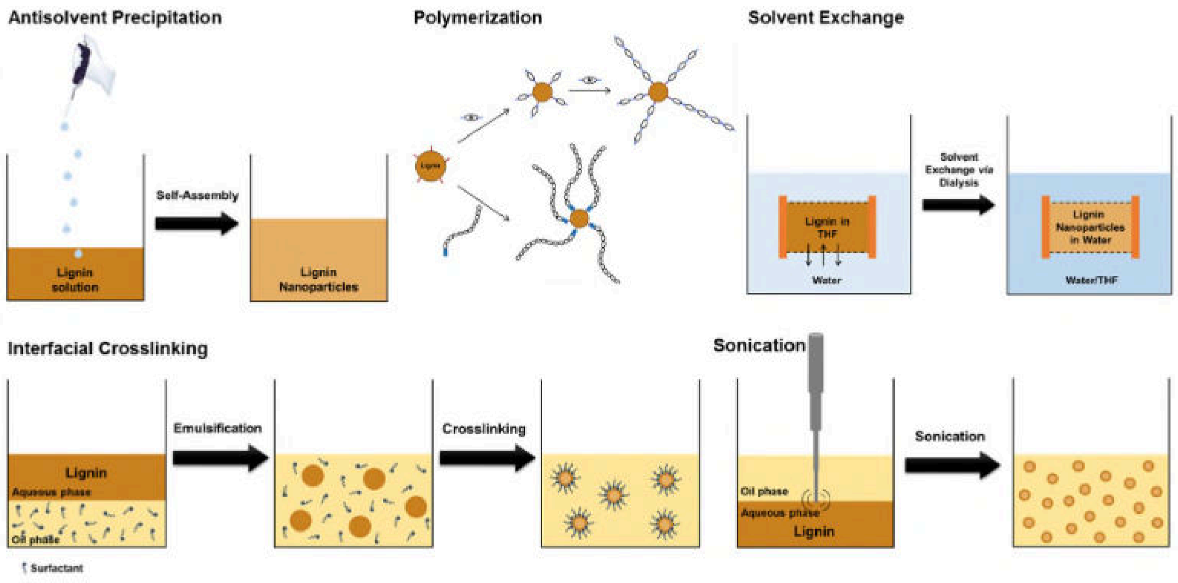


Figure 6. The different production processes of LNPs. Reproduced with permission from ref 57. Copyright 2018 Elsevier.

Lievonen et al. had used a solvent exchange method to make spherical LNPs. In this method, lignin was dissolved in tetrahydrofuran (THF). Subsequently, water was added without any chemical modification of lignin. [67] According to the results of the predialysis lignin amount, the diameter of prepared nanoparticles varied in a variety of 200-500 nm. Moreover, a nanoparticle suspension was gradually added into the PDAC solution. Thus, the surface of LNPs had been functionalized by the adsorption of an oppositely charged PDAC. Prepared LNPs were proposed to be utilized in nanocomposites, and antimicrobial materials as well as drug delivery applications.

Lintinen et al. had synthesized LNPs with iron to obtain particles which have different sizes from 50 to 400 nm (Figure 7). [68] In this method, lignin was dissolved in THF. Then, this solution was mixed with $Fe(OiPr)_3$. A condensation reaction was initiated via this solution. The reaction was terminated by putting H_2O into a solution. At the end of the procedure, iron(III)-complexed LNPs were prepared. Besides, nanoparticles prepared with $Fe(OiPr)_2$ or $Fe(OiPr)_2/Fe(OiPr)_3$ exhibited different magnetic characteristics closely related to the volume and form of these particles. As a result, LNPs might be utilized to make magnetic nanoparticles having antibacterial as well as biocompatible characteristics.

Figueiredo et al. had reported on the improvement of three types of spherical LNPs using the solvent exchange method (Figure 8). [69] These three types had been prepared as pure LNPs (pLNPs), [67] Fe-LNPs [68], and Fe_3O_4-LNPs. Fe_3O_4-LNPs had been produced by adding a kind of lignin mix into oleic acid-coated with Fe_3O_4 nanoparticles. The superparamagnetic behavior of synthesized materials was promised to be used for the cure of cancer. [69] LNPs showed less cytotoxic effect over different cancer cells. Besides, they exhibited less hemolytic rates after 12 hours' incubation with red blood cells. Thus, pLNPs were used for the encapsulation of hydrophobic drugs. The encapsulation developed releasing systems and increased the anticancer role. Consequently, it presented significant properties for drug delivery and biomedical applications. Especially for cancer therapies, LNPs have enabled the researchers to modulate compartments to make cellular uptake easily possible in target cells. [69]

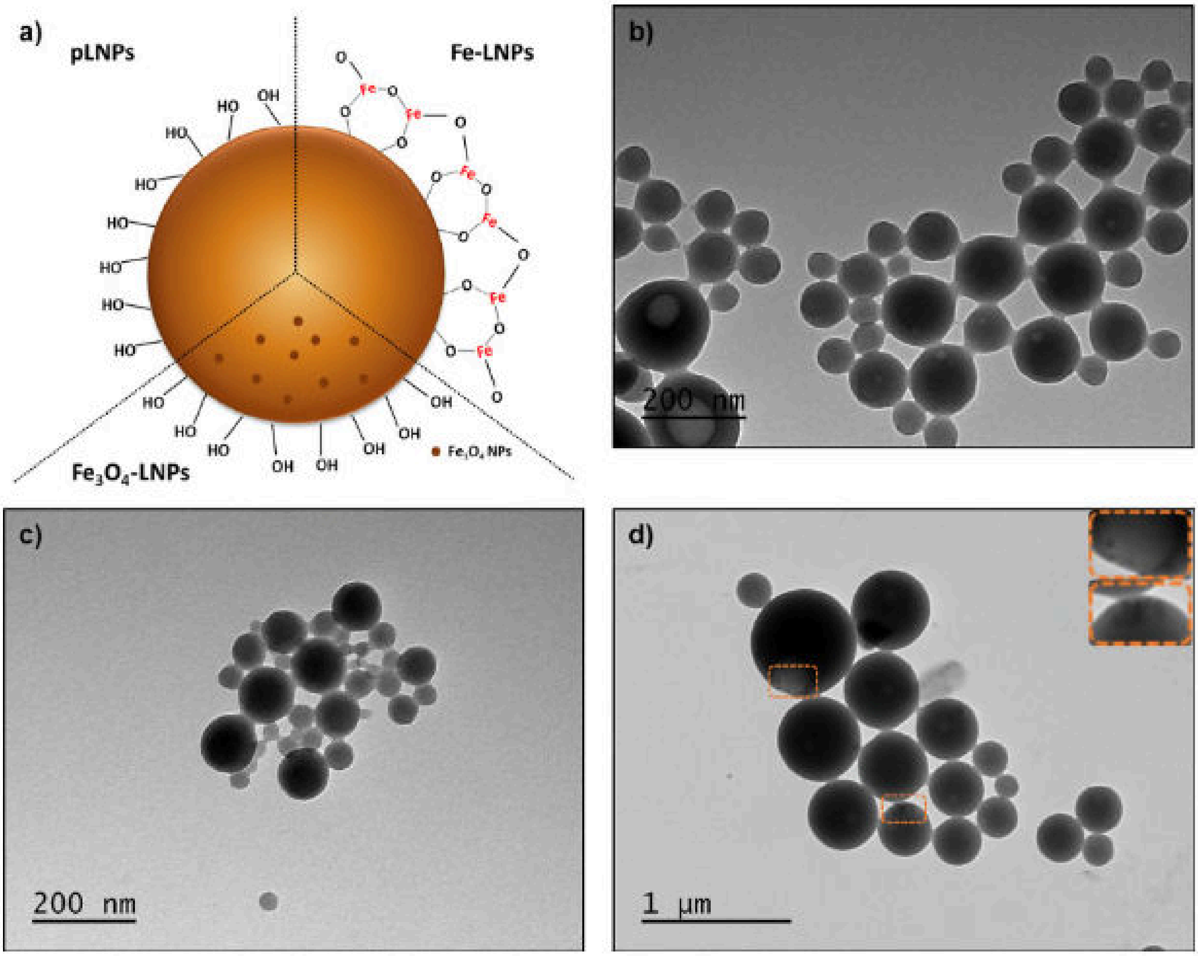


Figure 7. (a) The schematic representation of LNPs. TEM micrographs of (b) pLNPs, (c) Fe-LNPs and (d) Fe_3O_4-LNPs and magnification of the Fe_3O_4-NPs in LNPs. Reproduced with permission from ref [68]. Copyright 2017 Elsevier.

Lignin nanocapsules had been synthesized by Li et al. In their method, lignin was found to be first completely soluble in ethanol. After that, H_2O was mixed in the solution. [70] The size of the prepared nanocapsules was changeable in a variety of tens to hundreds of nanometers. These nanocapsules were suitable for different applications due to their excellent properties such as biodegradability, low cost, biocompatibility, and environmentally friendly characteristics.

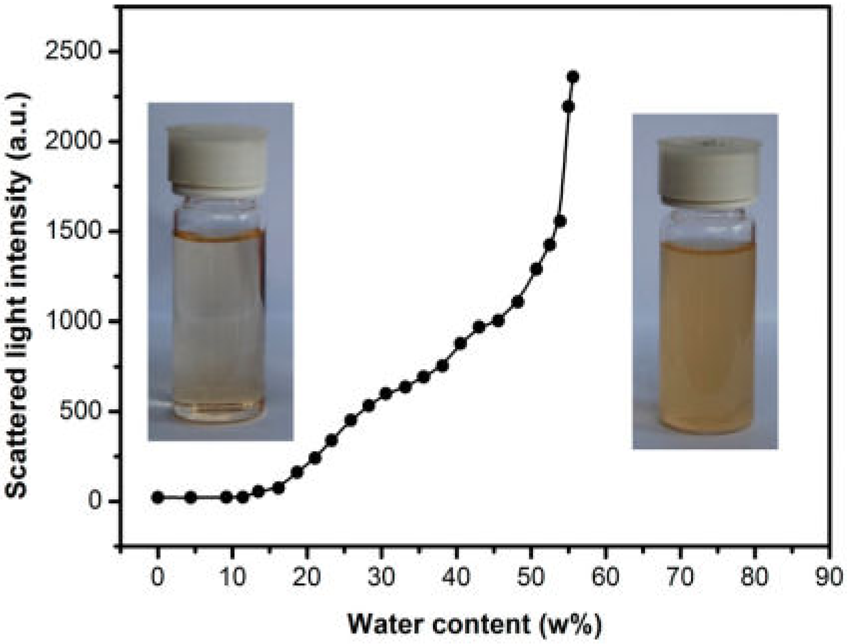


Figure 8. The scattered light intensity (a.u.) versus water content (w%) in the solution graph with kraft lignin in ethanol (left) and kraft lignin nanocapsules in ethanol and water solution (right)[69]. Reproduced with permission from ref 69. Copyright 2016 Elsevier.

Chen et al. had reported their studies on the production of pH-responsive lignin capsules. They had used the interfacial miniemulsion polymerization method. [71] Firstly, they vigorously mixed oil phase including azobisisobutyronitrile (oil-soluble initiator), butyl acetate, hexadecane (co-stabilizer), and trimethylolpropane tris(3-mercapto propionate) (cross-linker) with H_2O phase including lignosulfonate with/out sodium dodecyl sulfate (SDS). Thus, droplets made from oil-in-water mini emulsions were prepared using an ultrasonicator. Then, for forming nanocapsules, the cross-linking was added into lignin. By dissolving coumarin-6 in butyl acetate, nanocapsules were also prepared using the same procedure. Finally, the diameters of capsules were found to be varied in the range of 50-300 nm. Coumarin-6 has a hydrophobic character and its release from the capsule shell was achieved in changing pH because of β-thiopropionate cross-linkings (Figure 9). The lignin capsules are one of the desired materials especially in controlled releasing applications for drugs, antioxidants, and essential oils.

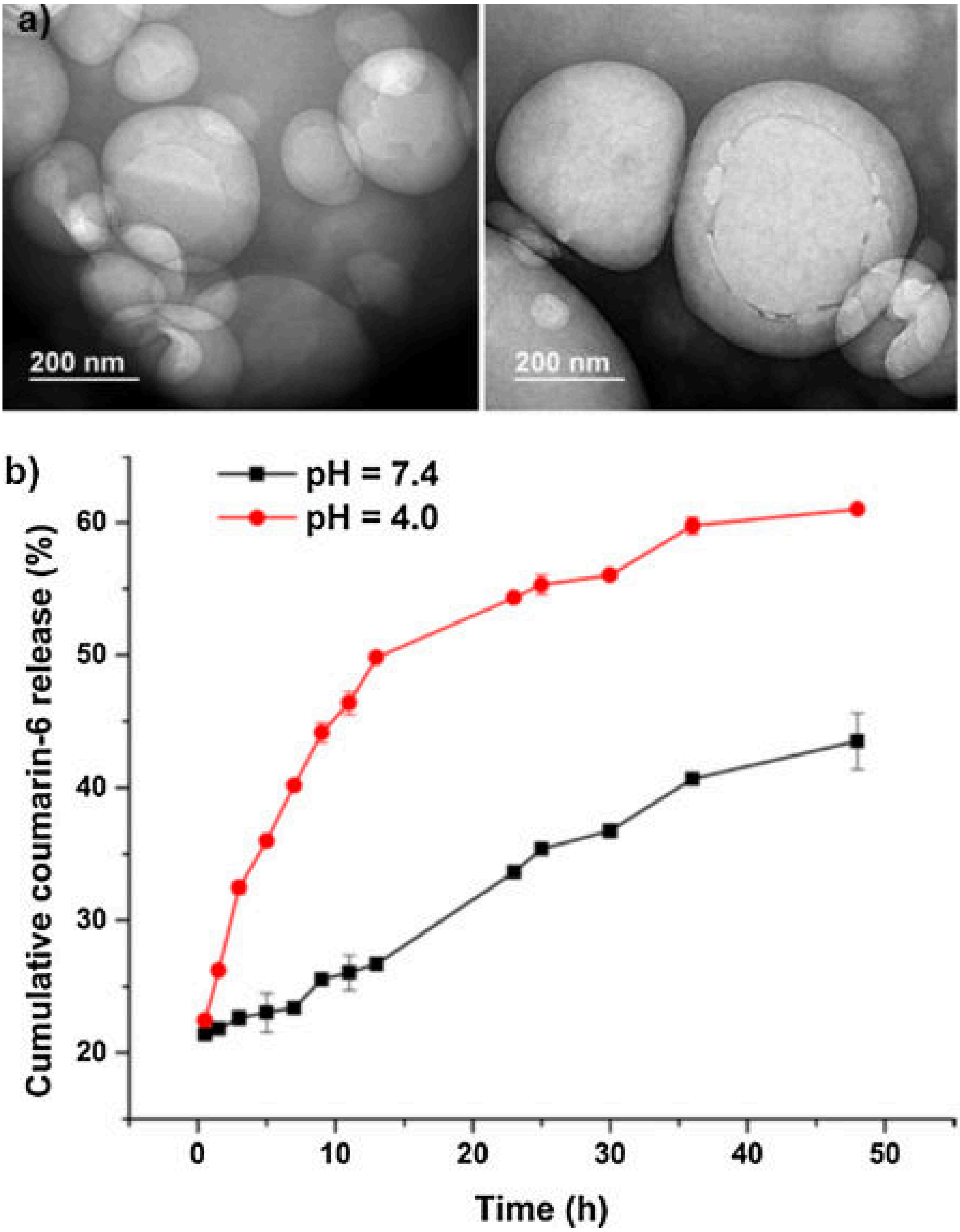


Figure 9. (a) TEM micrographs of lignin capsules. (b) Releasing of coumarin-6 for lignin nanocapsules (pH 4.0 and pH 7.4). Reproduced with permission from ref [71]. Copyright 2016 American Chemical Society.

Graphene-based nanocarriers exhibit a large specific surface area. Besides, they also prevent drugs from the early release of target cells. On the other hand, agglomeration in aqueous solutions is a big problem. In the research of Luo et al., graphene oxide (GO) had been homogenously embedded into 3-D porous networks of bacterial cellulose (BC) to make a new BC/GO nanocomposite drug nanocarriers (Figure 10). [72] In this study, ibuprofen (IBU) was loaded onto BC/GO nanocomposites for the first time. The characterization results revealed successful drug loading onto these BC/GO nanocomposites. Drug releasing researches indicated that IBU@BC/GO releasing corresponds to a non-Fickian diffusion mechanism. A significant feature of this BC/GO nanocarriers was also that they had higher cell viability compared to BC.

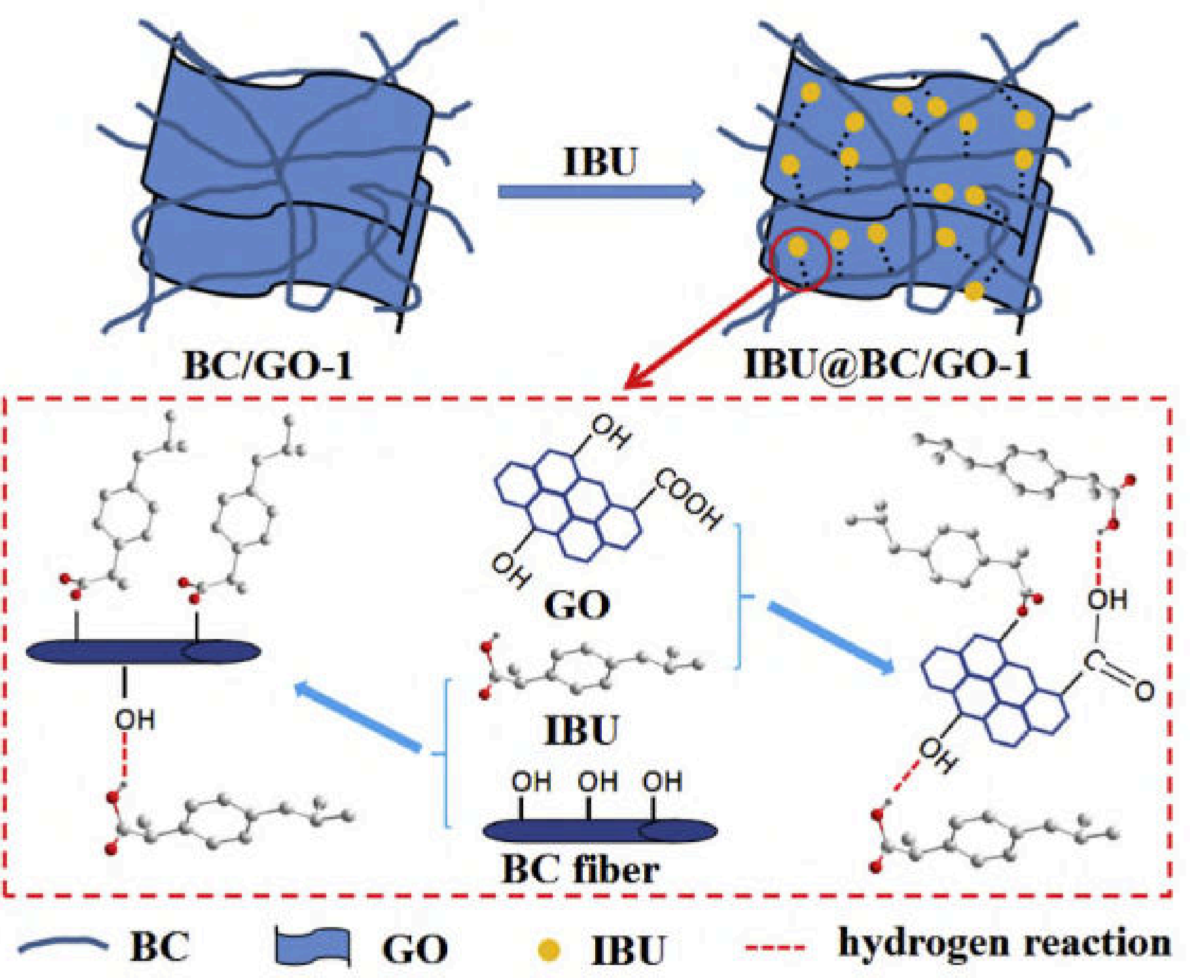


Figure 10. The mechanism of surface interactions between bacterial BC/GO and IBU. Reproduced with permission from ref [72]. Copyright 2017 Elsevier.

L-asparaginase (L-asparagine amino hydrolase, E.C 3.5.1.1) is one of the most widely used drugs in leukemia chemotherapy.[73] This drug is immobilized to various materials due to the side effects and short half-life of the enzyme. Natural and/or hybrid materials are the most preferred carriers. For instance, calcium-alginate/multi-walled carbon nanotube hybrid composite beads were used for immobilization of L-asparaginase.[74] After immobilization, L-ASNase displayed better stability and reusability. The authors reported that calcium-alginate/multi-walled carbon nanotube hybrid composite beads are promising carrier matrix for L-ASNase such as commercial enzyme-drugs. In another work, maltose functionalized magnetic core/shell Fe_3O_4@Au hybrid nanoparticle composite was synthesized for an efficient L-asparaginase immobilization [75]. According to the obtained results, pH and thermal stability of immobilized L-ASNase were significantly improved in comparison to the free enzyme-drug. Consequently, hybrid composites supports are good candidates for drug delivery or immobilization.

Samples of drug delivery applications of nanocomposites from bio-renewable resources are also given in Table 2 as summary information.

Table 2. Drug delivery applications of nanocomposites from bio-renewable resources

Nanocomposite	Applications	Releasing	Ref.
Hydroxyapatite (HA)/collagen alginate	Inducing the regeneration of bone and cartilage for *in vivo* models	Fibroblast growth factor-2	[58]
HA/CH nanocomposite	Drug-delivery matrix	Vitamins	[59]
Double layered-hydroxide polylactic acid	Releasing of an anti-inflammatory drug	Ibuprofen	[61]
Double layered-hydroxide xyloglucan	Slowly releasing of an anti-hypertensive agent	Enalaprilat	[62]

Lignin nanoparticles	Drug delivery	Benzazulene® and Sorafenib®	[64,65]
Silver-infused lignin-core nanoparticles	Antibacterial materials and drug delivery	Silver ions	[66,67]
Lignin nanoparticles with Fe_3O_4	Antibacterial materials and drug delivery	Oleic acid	[68]
Spherical LNPs	The encapsulation of hydrophobic drugs	Hydrophobic drugs	[69]
pH-responsive lignin capsules	Controlled releasing applications for drugs, antioxidants, and essential oils	Coumarin-6	[71]
BC/GO nanocomposite	Controlled releasing of an anti-inflammatory drug	Ibuprofen	[72]

2.2. Tissue Engineering Applications

Tissue engineering aims to support tissue regeneration and growth of healthy cells or create materials that can be replaced. Materials to be developed in this field should include specific characters for application areas in terms of either morphological or structural sense. In this context, nanocomposites that are very good at mimicking the natural morphology of extracellular matrix surrounding cells are very suitable for the promotion and repair of tissue structures (Figure 11). The extracellular matrix has three main characteristics. [76] The first of them, the extracellular matrix is the sum of macro-sized molecules, for example; protein and saccharides. Secondly, macromolecules in extracellular matrix exhibit **fibre** structures that have a length/diameter ratio higher than one hundred. Lastly, macromolecules in the extracellular matrix are generally less than 500 nm of diameter in nanoscale. In this context, it is clear that especially the extracellular compounds containing renewable bio-macromolecule structures and similar-sized nanocomposites have attracted great interest in this area.

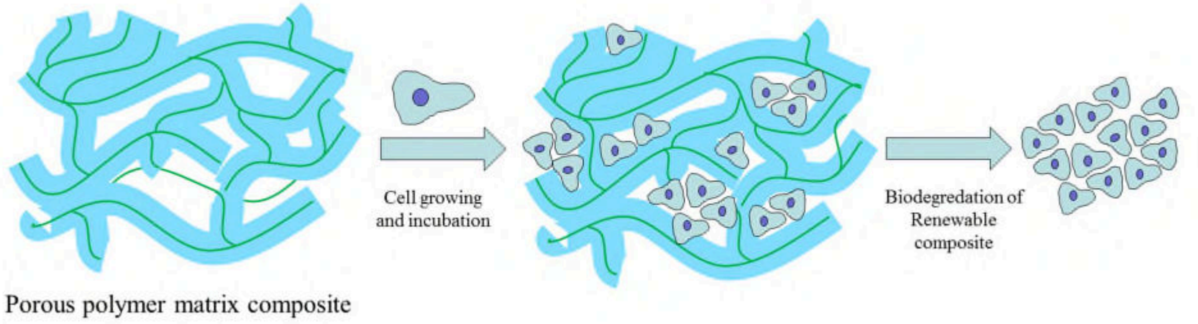


Figure 11. Schematic illustration of tissue engineering applications of porous bio-renewable composites.

When we look in general to the field of tissue engineering, we can say that the most large-scale application of nanocomposites generated from bio-renewable resources is bone-tissue engineering. Natural bone occurs by the hierarchical organization of collagen protein fibres, HA mineral nanocrystals, and proteoglycans in nanoscale. [77] Collagen allows bone a structural matrix and flexibility with a high level of strength. Bone stiffness and tensile strength are provided by HA nanocrystals. Collagen, whose length of a fibre is 500 nm, is a triple-helical protein and these fibres form the structure of each collagen helical chain having 10 nm in length. During the recreation of the natural structure of bone, nanocomposites are formed by synthesizing polymer building blocks and HAs. [78] In clinical orthopedics, biodegradable and bioabsorbable nanocomposites that have to induce and encouraging novel bone formation are essential for bone regeneration in the area of implementation. Furthermore, nanocomposites for bone tissue engineering should also include enough microporosity helping novel tissue formation. For this purpose, HA-collagen nanocomposite material prepared from bio-renewable resources was synthesized at 37 °C and pH 7. It had been determined that under these physiological conditions, collagen fibrils and HA nanoparticles led to a porous structure at the same time. [79] These kinds of scaffolds have been found to show high elasticity. Fortunately, they have also been successfully implanted into animals to repair and reconstruction of bone defects. [80] Scaffolds material can gain high flexibility and shape memory properties with ice crystal growth and its subsequent dry ice of 3-D pore structure of HA-collagen nanocomposites. [81] The homogeneous structure of CH-HA composites has been produced by the coprecipitation method. [82] Eventually, these composites can be implanted into bone marrow without any inflammation response. Besides, novel bone growth has occurred around implanted CH-HA nanocomposites. Another application from renewably resourced nanocomposites was that HA-gelatin nanocomposite fibres were prepared by a process comprising electrospinning followed by precipitation. [83] It was determined that bone derived osteoblast cells grew and multiplied by adhering on this prepared gelatin-HA fibre mesh. These nanocomposites can also allow the development of functional activity and differentiation of osteoblast cells. [84]

Besides, HA/CH-gelatin network composites composed of three components were produced by phase separation method. [85] These composites have shown that osteoblasts hold this network and the extracellular matrix containing collagen I and proteoglycan were synthesized. Then, these HA/CH-gelatin network composites were found to induce bone-tissue generation. Furthermore, the composite including three components of gelatin/montmorillonite (MMT)-CH was produced. [86] It had been found that mouse bone marrow-originated stromal stem cells adhered to gelatin/MMT-CH membranes to proliferate.

Nanocomposites formed by the alginate and HA polysaccharides are used for bone regeneration. In this structure, alginate serves as a polymeric sponge for tissue engineering scaffolds. Thus, biomimetic nanocomposite materials were formed by directly core-forming of apatite crystals on the spontaneous alginate chains allowing the development of osteoblast. [87] Furthermore, in another work silk fibroin and HA nanocomposites had been synthesized with the method of coprecipitation. [88] Besides, three-dimensional scaffolds made of porous structured silk fibroin network/nano-HA composites were produced. It had been reported that the silk-HA scaffold increases the vitality of osteoblasts as well as being tissue compatible with osteoblasts. Moreover, it had been shown that silk-HA fibril components forming in the scaffold interact with cells and layers and locate in the extracellular matrix. [89] In tissue engineering applications, nanocomposites were developed using bio-renewable resources of proteins (BSA, casein, etc.) and formed with nanocrystalline structured HAs. [90,91]

In another work, a uniform blend of chitin and poly (butylene succinate) (PBS) composite containing Chondroitin sulfate nanoparticles (CSnps) was developed and characterized. [92] The porosity of the blend scaffold increased with the incorporation of CSnps. For the proper gas and nutrient exchange, optimum porosity and controlled swelling were achieved. Human dermal fibroblasts attachment and proliferation also increased due to the macro-porous and bioactive nature of the nanocomposite. These nanocomposites may be utilized as a scaffold in skin tissue engineering (Figure 12). Poly-L-lactide (PLA) based nanocomposites are located in the elimination of bone tissue damages in tissue engineering. PLA in bone tissue is insufficient to withstand load resistance applications. Therefore, increased mechanical properties were obtained by doping of nanodopers such as fibres, clay, and HA to the structure of PLA based nanocomposites. It is an example of improving the flexural modulus and the strength of PLA-based nanocomposites by nano-reinforcement. [93] It had also been demonstrated that the addition of silica nanoparticles and organically modified MMT into the PLA matrix enhanced the mechanical and thermal properties. [94] It had been proved that such bio-renewable resourced PLA nanocomposites are successful in the bone repair processes in animal models. [95]

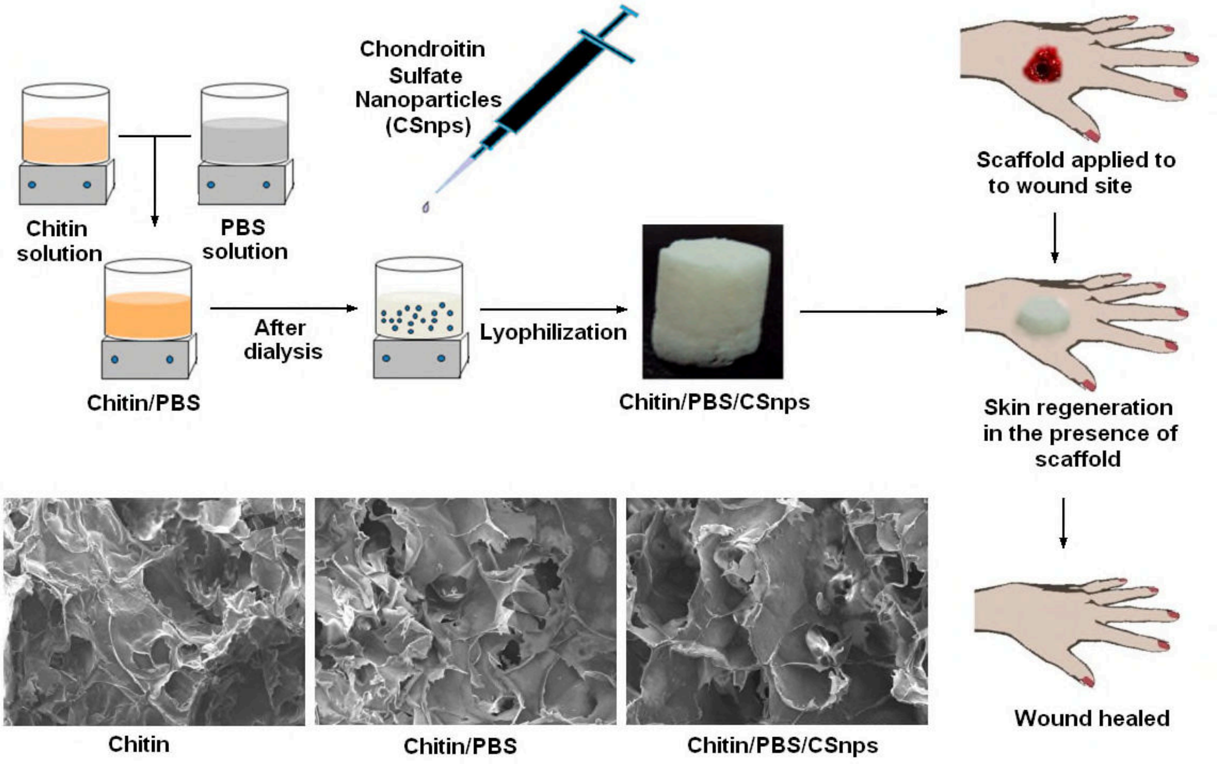


Figure 12. Schematic representation of preparation, scanning electron microscopy (SEM) micrographs and application of Chitin/PBS/CSnps scaffold. Reproduced with permission from ref [92]. Copyright 2014 MDPI.

The widest range of nanocomposites from bio-renewable resources in orthopedic applications is to repair bone with a certain part of the damage. Bone is a kind of nanocomposite including a polymer matrix (generally collagen) with nano-sized ceramics (generally HA). Recently, scientists related to the area in bone growth have said that once nanomaterials were prepared to mimic bone in terms of its proper characteristics, we would be able to have advanced osteoconductivity. [96,97] Du et al. [96] had made nanocomposites consisting of HA/collagen, which creates porous microstructures. Since these structures are similar to bone in nanoscale, these kinds of materials help the formation and growth of bone. Furthermore, HA in the bone structure has another unique characteristic because of not having a big size and small surface. Particularly, Webster et al. [97] had shown an important increment in preliminary protein adsorption. Consequently, advanced adhesion in osteoblastic was observed compared with the conventional ceramic materials (HA, alumina, and titania). [98–100] The surface characteristics of scaffolds that are similar to natural bone in terms of the surface grain sizes will help in the growth of novel bone at the cells/biomaterial surface. Thus, the design of next-generation scaffold structures has to unify different nanosized materials. Implants that cause osteointegration by promoting cell and tissue interactions are required. Superficial properties are mostly dependent on any material' size. Therefore, nanosized materials generally possess high surface areas having some defects, which are currently unclear for the medical area. Roughness on the surface affects the relationships in adhesion, adsorption, and activity of proteins. [97,101–103] Liu et al. [104] reported that titania/poly(lactic-co-glycolic acid) (PLGA) composites showed osteoblast adhesion and calcium-containing mineral deposition. In another work, [105] the authors showed high protein adsorption on nano-HA/PLA scaffolds compared to micro-HA/PLA scaffolds for osteoblast adhesion. A lot of researches focuses on the detailed points of elevated osteoblastic for nanomaterials. Some *in vitro* studies have shown the grain size in the nanometer scale for enhancing ceramic cytocompatibility as the primary parameter. For instance, ceramic formulations, and large grain size, elevated the adhesion of osteoblasts and diminished the adhesion of fibroblasts, which are the cells that are responsible for fibrous encapsulation and callus formation situations which are closely related to the success and failure of the implant, had been observed on nanosized HA alumina and titania. [98] Decrease of the alumina grain size had elevated osteoblast adhesion and had decreased in fibroblast adhesion. Researches of the main points showed that the conformation, amount, and activity of vitronectin, which is a kind of protein and has a role to maintain osteoblast adhesion, were closely related to the selection and increased the adhesion of osteoblasts on these new ceramics. Vitronectin is adsorbed into the small pores in nanocomposite ceramics. For instance, vitronectin adsorption had been 10% higher on nanocomposite compared to the alumina. [106]

Moreover, protein conformation has an important characteristic in the continuum of cell/cell relations. Increment in unfolded vitronectin was collected on nanocomposite ceramics. [106] It had been demonstrated with competitive inhibition studies that the unfolding of vitronectin supported the specific cell-adhesive epitopes, for example, the arginine-glycine-aspartic acid-serine sequence for enhancing the osteoblast adhesion. [106]

Nanosized biocomposites can be synthesized to achieve some physical properties such as compressive, bending, and tensile strengths which are like natural bone. It has been demonstrated that bio-composites containing nano-sized ceramic particles exhibit good mechanical behavior. McManus et al. [107] reported that the modulus of a blend of PLA composites having weight percent of 40-50 nanocomposites with HA, titania and alumina were much higher than composites that are currently being used in coarse-grained ceramics.

According to the mechanical deformation theory, if the grain size decreases, most of the interfacial regions increase the deformation amount compared to bulk materials with boundary change of grain and healing of diffusion in a short time. Therefore, ductility increases in nanocrystalline ceramics. Unlike conventional ceramics, nanocomposite ceramics present an elevated roughness depending on the decrease in size and pore diameters. Furthermore, because of great surface roughness and grain boundaries on their surfaces, nanocomposite ceramics show enhanced surface wettability.

A few studies have also exhibited utilization of lignin for advancement in current materials as aerogels, hydrogels, and nanofibres. [75–78] Diao et al. had performed research with the production of lignin-based copolymers by the ATRP technique. [111] Authors have used multiple graft polymer chains including polyN-isopropyl acrylamide (PNIPAAm), PEG, and polypropylene glycol (PPG) and a lignin core. In solutions, the copolymers exhibited thermogelling characteristics. Thermogelling behavior means that changing from a solution firstly to a hydrogel and later to a dehydrated gel by increasing temperatures (Figure 13). The block structure of the copolymers located in lignin is important for the formation of hydrogels. The hydrogel is obtained once the lignin-based PNIPAAm-block-PEG/PPG copolymer is utilized. On the other hand, once a lignin-based PNIPAAm-random-PEG/PPG copolymer is utilized, the formation of hydrogels wasn't obtained at any temperature. Moreover, thermogel copolymers showed less critical gelation amounts. In these concentrations, the PNIPAAm block is crucial to prepare gels. Also, PPG may help H_2O retention with the hydrophilicity/phobicity balancing. Thus, resulted in copolymer solutions had a higher thermogelling transition temperature. This phenomenon suggests that prepared hydrogels with the usage of stem cells can be beneficial especially for tissue engineering and drug delivery applications.

Quraishi et al. had synthesized alginate-lignin gels for the release of Ca^{2+} from the crosslinking of alginate–lignin. They had used CO_2 as an acidifier because CO_2 enables the gelation procedure with the help of solvent exchange and supercritical drying. [112] These alginate-lignin gels exhibited superficial and morphological properties as well as cytocompatibility and very good cell adhesion.

Figure 13. The preparation procedure of alginate-lignin hybrid aerogels for biomedical applications[111]. Reproduced with permission from ref 111. Copyright 2015 Elsevier.

Polymeric nano**fibre** matrices fabricated from lignin are novel materials that mimic the extracellular matrix for the future development in tissue engineering applications as scaffolds.

[113,114] Kai et al. had synthesized polylactic acid (PLA)–lignin copolymers by using PLA into alkylated lignin with ring-opening method utilizing in various proportions of lignin as 10–50%. [113] The research group reported that the resulting copolymers' PLA chain lengths were different. Then, these copolymers were mixed with poly-lactide (PLLA) to produce nanofibrous composites using the electrospinning technique (Figure 14). Obtained nanofibres presented well antioxidant activity and biocompatibility results being incubated with PC12, dermal fibroblasts, and mesenchymal stem cell lines.

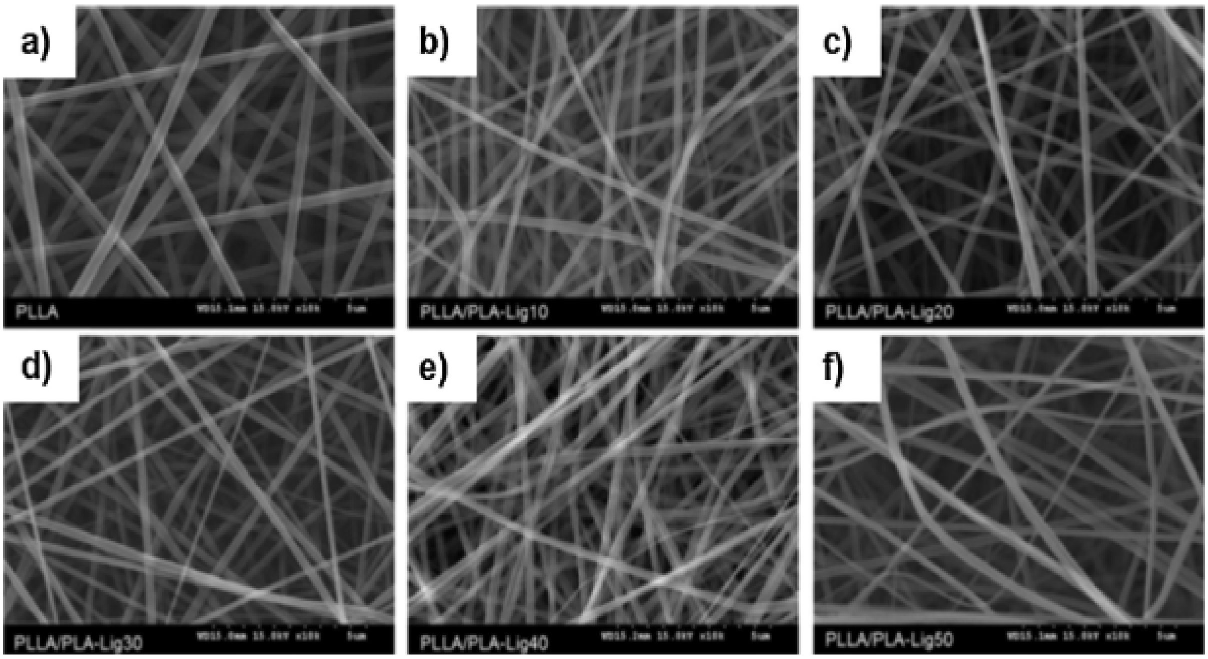


Figure 14. The SEM micrographs of nanofibres containing different ratio lignin: (a) PLLA; (b) 10%; (c) 20%; (d) 30%; (e) 40%; and (f) 50%. Reproduced with permission from ref [113]. Copyright 2016 American Chemical Society.

Mezzenga et al. [115] developed a novel method to prepare a hybrid nanocomposite using amyloid fibrils and hydroxyapatite which exhibits a couple of bone-mimetic properties. Physical characteristics of the new hybrid nanocomposite were far better than clinically used bone types of cement. Besides, human trabecular bone-derived pre-osteoblastic cells were used to show effective adherence and growth on the hybrid nanocomposite including amyloid fibrils and hydroxyapatite.

Maji et al. [116] prepared a graphene-amyloid hybrid nanocomposite film for alignment and differentiation of cells on glassy-like materials to mimic in vivo conditions using a novel type of scaffold. Human neuroblastoma cells were used because of ease of observation of the conductive nature and cellular alignment of these types of cells.

As being seen from all of these examples, nanocomposites having two or three components derived from bio-renewable resources are generally used particularly in bone tissue engineering. In this regard, bio-renewable sources such as polysaccharides and proteins are very important. Especially in terms of tissue engineering applications, it is clear that bio-renewable-based nanocomposites would be an important research area in the near future.

Samples of tissue engineering applications of nanocomposites from bio-renewable resources are also given in Table 3 as summary information.

Table 3. Tissue engineering applications of nanocomposites from bio-renewable resources

Nanocomposite	**Fabrication Techniques**	**Applications**	***In Vitro* Studies**	**Ref.**
HA-collagen	The biologically inspired mineralization process	Bone tissue generation	Human expanded chondrocytes and sheep bone marrow stromal cells	[79]
CH-HA	Coprecipitation method	Tissue regeneration	-	[82]
HA-gelatin nanocomposite **fibre**s	Electrospinning followed by precipitation	Guided tissue regeneration	Bone derived osteoblast cells	[83]
HA/CH-gelatin network	Phase separation technique	Bone-like tissue formation	Rat calvaria osteoblasts	[85]
Gelatin/montmorillonite (MMT)-CH	Solution intercalation process	Tissue engineering	Mouse bone marrow-derived stromal stem cells	[86]
Alginate-HA polysaccharides	Neutralization synthesis	Bone replacement needs and	Osteoblast-like cells (MG-63)	[87]

		drug-delivery devices		
Silk fibroin-HA	Coprecipitation	Tissue engineering	-	88
Chitin-poly (butylene succinate) (PBS) with chondroitin sulfate nanoparticles	Ionic gelation method	Skin tissue engineering	Human dermal fibroblast cells	92
Titania/poly(lactic-co-glycolic acid) (PLGA)	Multiple-point BET method	Bone tissue engineering	Human osteoblast cells	104
Polylactic acid (PLA)–lignin copolymers	Ring-opening method	Tissue engineering scaffolds for locally attenuating cellular oxidative stress	Rat adrenal gland cells (PC-12), dermal fibroblasts, and mesenchymal stem cell lines	113
Amyloid-Hydroxyapatite	The “bottom-up” approach	Tissue engineering	Human trabecular bone-derived pre-osteoblast cells	115
Graphene–Amyloid	Chemical oxidation of graphite using a modified Hummers method	Cell alignment and differentiation	Human bone marrow neuroblastoma cells (SH-SY5Y)	116
Amine functional n-HA/chitosan	Freeze-drying method	Bone tissue engineering	Human bone marrow mesenchymal stem cells	117
Aspirin-loaded (graphene oxide/chitosan - hydroxyapatite)	Layer-by-layer assembly technology combined with biomimetic mineralization method	Bone tissue engineering	Mouse mesenchymal stem cells	118
Bacterial cellulose/silk fibroin sponge	Soaking, shaking, and freeze-drying	Tissue engineering	Mouse fibroblast cells (L-929) and Chinese hamster fibroblasts (V79 cells)	119
Carbon nanotubes/chitosan/glycerophosphate	Freeze drying	Bone tissue engineering	Osteoblast-like cells (MG-63)	120
Chitosan/PVA/hydroxyapatite	Electrospinning	Periodontal regeneration	VERO cell line of epithelial cells	121

Chitosan-chitin nanocrystals	Freeze drying	Bone tissue engineering	MC3T3-E1 osteoblast cells	122
Chitosan-graft-poly(acrylic acid-coacrylamide)/hydroxy-apatite	Multistep freeze-drying method	Implants and drug carriers in bone tissue engineering	Human fibroblast gum (HuGu) cells	123
Dexamethasone-loaded poly(glycerol sebacate)PCL/gelatin	Coaxial electrospinning	Soft tissue engineering	Gingival fibroblast cells	124
Gelatin collagen bioactive glass	Freeze drying	Myocardial tissue engineering	Endometrial stromal stem cells and mouse fibroblast cells (L-929) cells	125
Keratin-modified bacterial cellulose	Fermentation	Skin tissue engineering	Human skin keratinocytes and human skin fibroblast cells	126
Multilayer scaffold of PLA, sulfated cellulose nanocrystals and phosphate cellulose nanocrystals	Thermally-induced phase separation	Cartilage tissue engineering	Human fetal chondrocytes of second passage (primary cells)	127
Poly(ethylene glycol)-grafted cellulose nanocrystals incorporated in PLA	Electrospinning	Bone tissue engineering	Human mesenchymal stem cells	128
Chitosan-modified montmorillonite	Solvent casting and particulate leaching	Tissue engineering	Simulated body fluid	129
Polyacrylamide grafted cellulose and hydroxyapatite	Freeze drying	Bone tissue engineering	Human fibroblast gum (HuGu) cells	130
Polyamide-6,6 blended with biopolymer chitosan	Electrospinning	Tissue engineering	Pre-osteoblast (MC3T3-E1) cells	131
$SrAl_2O_4$: $Eu^{2+}Dy^{3+}$ /chitosan-Poly caprolactone	Electrospinning	Retinal tissue regeneration	Murine retinal progenitor cells	132
Starch/ethylene vinyl alcohol/forsterite	Sol-gel method and shaking	Bone tissue engineering	Simulated body fluid and osteoblast-like cells (MG-63)	133
Zirconium oxide doped chitosan-organically modified montmorillonite-hydroxyapatite nanoparticles	*In situ* cationic polymerization technique	Bone tissue engineering	Osteoblast-like cells (MG-63)	134

2.3. Gene Therapy Applications

Biomaterials present significant potentials for many biomedical areas. For controlled gene delivery applications, much interest and focus are on biodegradable cationic polymers. Gene therapy applications have great potentials for curing different important illnesses. However, the main hindrance is a safe and efficient vector requirement for gene delivery. Biosafety issues such as oncogenicity, cytotoxicity, and immunogenicity of these viral vectors are still uncertain, yet. Otherwise, non-viral gene delivery vectors such as cationic polymers would overcome the handicaps.

Lipid-based bio-renewable sources can be easily self-regulated by supramolecular interactions and form stratified, tubular and spherical structures (Figure 15). These structures are very suitable alternatives for composites obtained from bio-renewable sources. In particular, composites obtained from lipid/DNA structures are very important. In gene therapy, renewably resourced nanocomposite structures have received substantial attention recently. In this context, lipoplexes and polyplexes are intensively investigated in gene therapy. Lipoplexes had been prepared to make either large aggregates surrounding with thin fibres or condensed DNA coating with a lipid bilayer.

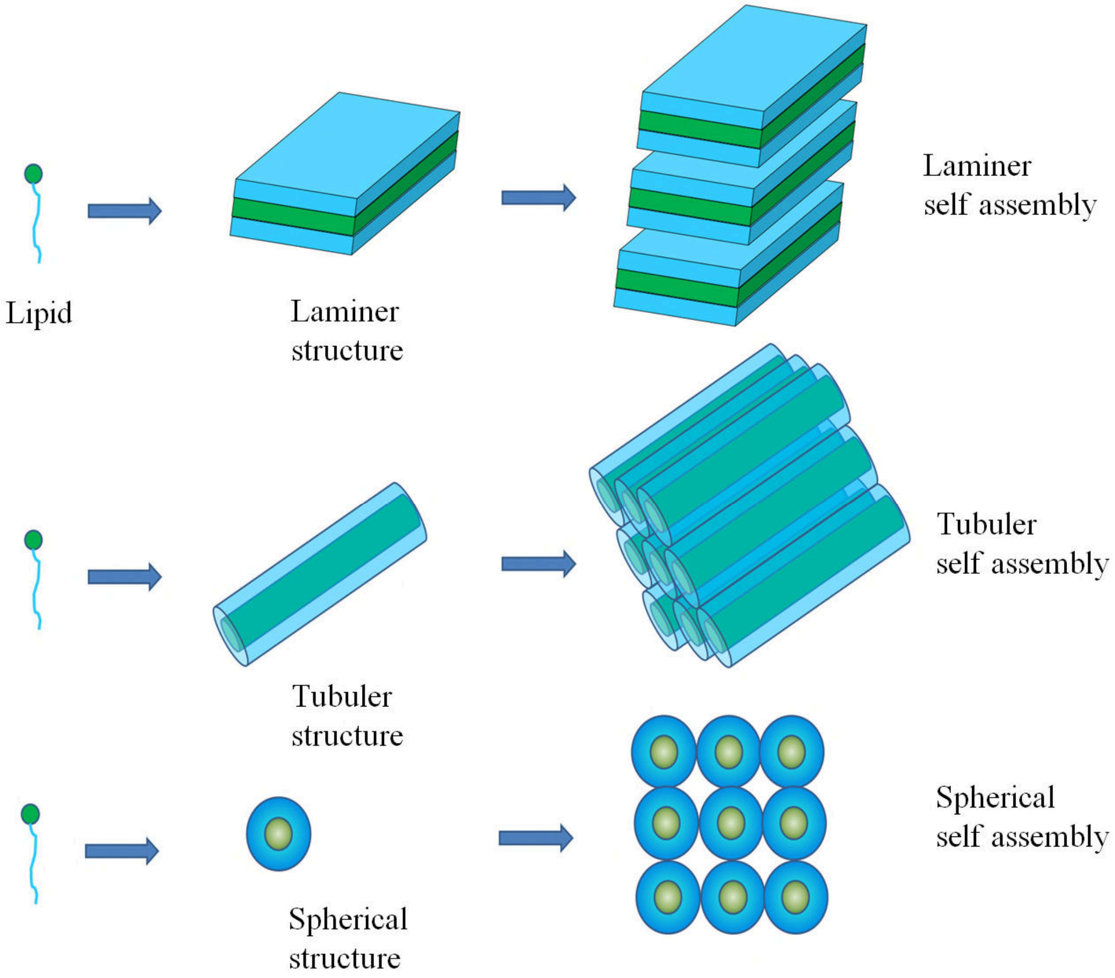


Figure 15. The schematic diagram of supramolecular self assembles of lipid-based structure for bio-renewable composites.

Similar to the structure of micelle complexes, the liposomes which stick to DNA strands are differently charged polyelectrolytes. [135] Not only the supramolecular structures but also the thermodynamic stability of lipoplexes had been researched. [136–140] For hexagonal packing of DNA coated by these lipids, the “sliding columnar phase” had been especially suggested Without losing the orientation of the chains, this is a kind of coherence between DNA molecules in neighboring layers. [141]

Most of the cationic polymers are well-known for the attachment of DNA in the preparation of polymer/DNA complexes and positively charged surfaces causing measurable transfection activity *in vitro*. After a couple of repeated administration, other clinical transfections are restricted due to the low transfection efficacy and high cytotoxicity. An et al. [142] have reported the preparation of a new 4-arm PEG-b-poly(disulfide histamine) copolymer of PEG vinyl sulfone and amine-capped poly(disulfide histamine) oligomer (4-arm PEG–SSPHIS) for cancer therapy. The synthesized copolymer had been found to condense DNA into nanoscale polyplexes. The transfection experiments had demonstrated that under acidic conditions, polyplexes of 4-arm PEG–SSPHIS showed increased transfection efficacy.

LNPs have been utilized for gene delivery applications. Ten and his colleagues have reported their studies on the synthesis of lignin nanotubes. [143] They had used nanopore alumina membranes. Lignin was found to interact with amine groups located on the alumina membranes nanoporous surface. By using a catalyst, the polymerization of the monolignols was achieved. At the end of the reaction, phosphoric acid was used for the preparation of lignin nanotubes. The physicochemical characteristics of nanostructures were closely related to the composition, and origin as well as the extraction method of lignin. These properties were found to change both the size and reactivity of lignin. The lignin nanostructures exhibited high properties in biocompatibility as well as DNA binding capacity. Both characteristics are appropriate and beneficial to make these nanotubes suitable for delivering genes.

2.4. Antimicrobial Applications

Nanocomposites obtained from bio-renewable resources are also being designed for antimicrobial purposes. In these nanocomposites, polysaccharides and proteins have been commonly used as the main matrix elements. Inorganic metals/ metal oxides such as Au, Ag, TiO_2 and antibacterial organic compounds like essential oils are used as antibacterial agents. In this area, especially food packaging and surface coating materials have come to the fore. The most important reason for this is the biodegradable characteristics of discarded bio-renewable materials produced from plant and animal resources. For this purpose, films and coatings made from biopolymers can be prepared from different proteins, for example; casein, collagen, gelatin, soy protein, and wheat gluten. [137,138] The prepared material acts to block the passage of moisture, gas, and solvent as a selective barrier as well as increasing food safety with the antimicrobial property. However, having some disadvantages such as cost and the mechanical strength of such nanocomposites limits their use. [139–141] In particular, to eliminate the mechanical disadvantages, metal oxide nanoparticles, nanoclay, metal, carbon nanofibres, and nanotubes are doped. [138,142,144–146]

Nanocomposites with Zein protein are one of the examples of antibacterial food packaging from bio-renewable resources. Zein is abundant in corn gluten meal and it's all features are very well known. [147,148] Especially, at low water activity films obtained from maize Zein protein are very brittle and its mechanical characteristics are importantly affected by moisture. With the participation of plasticizers such as glycerol and PEG, the fragility and processability properties of the corn Zein films have been improved. [147,149–151] Nanoenhancers are used to increase the mechanical performance of corn Zein films. The other biopolymer research for film applications is whey protein isolate, which is the byproduct of cheese making industry. Although these protein films show stable mechanical properties, they show poor tensile strength along with high-water vapor transmission in packaging applications related to the food. [145] Whey protein-polymer matrixes had been reinforced by using nanofillers such as nano clay. [152] In another study, the mechanical behaviors of WP and corn Zein films had been increased via SiO_2 coated TiO_2 particles as nanoenhancers. [153] Films and coatings for packaging applications with antimicrobial function have been presented as an effective method to control microbial contamination in ready-made food. [154] Due to the photocatalytic activity of TiO_2 nanoparticles exhibiting protective properties against microorganisms transmitted by food, they show antimicrobial properties as TiO_2/SiO_2 nanoenhancers under UV light. The addition of TiO_2/SiO_2 nanoenhancers to biopolymer matrixes like proteins not only incorporates antimicrobial function but also enhances the mechanical strength of the films. From another point of view, nanocomposites that have inhibitory effects on *E. coli* and *Salmonella typhimurium* especially in the packaging of meat had been prepared by adding EDTA to bio-renewable films comprising of nisin and lysozyme.

CH has antimicrobial [155], antiviral [156] and antitumoral [157,158] activities. Since CH has excellent characteristics that interact with the human body, in the field of biomaterials it has numerous applications such as bioactivity, chemotactic movement, mucoadhesion, enzymatic biodegradability and epithelial permeability allowing the different cell to adhere and proliferate [159]. Even though the antimicrobial mechanism has not been fully understood, there is a common conviction that CH interaction with the negatively charged cell membrane leads proteins and other cell structures to leak outside of the cells. CH coating of vegetables and fruits with a film provides antimicrobial preservation extending the product's shelf-life. [159] It had been determined that chitin and CH increased the movement of biological organisms that have plaque control such as Bacillus and Trichoderma species and they were also good candidates for the encapsulation of biocides. [160] CH has some problems such as low solubility and miscibility with other positively charged polyelectrolytes. Therefore, chitlac (1-deoxylactit-1-yl CH), lactose-substituted CH, had been formed. Then, these branched polysaccharide nanosilver structures were used in the production of CH nanoparticles. Hydrogels were prepared by mixing the solution of alginate with CH-nanoparticles (Figure 16). It had been demonstrated that these hydrogels exhibit antibacterial properties against *S. aureus*, *S. epidermidis*, *E. coli*, and *P. aeruginosa* microorganisms. [156]

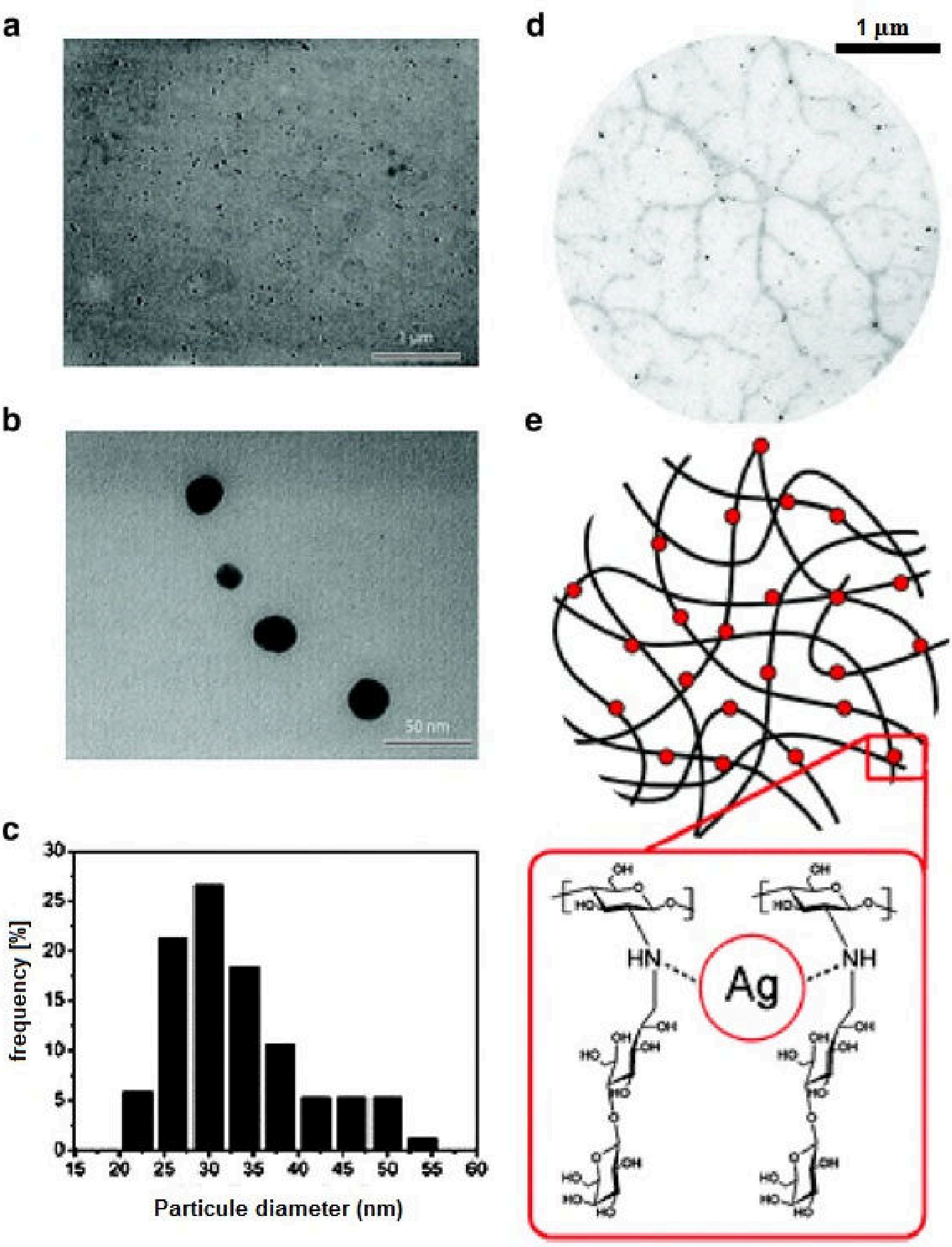


Figure 16. The TEM micrograph of AgNPs dispersed in chitlac, which is a natural saccharidic polybase, at different magnifications (a,b); The particle size of AgNPs based on the TEM micrograph c); The TEM micrograph of AgNPs formed on the polymeric chains of chitlac. By using lead citrate and uranyl acetate solution, chitlac chains had been stained (d); The diagrammatic illustration of polymeric chains of chitlac. Nitrogen atoms had been utilized for the coordination and stabilization of AgNPs (e). Reproduced with permission from ref [161]. Copyright 2009 American Chemical Society.

Cellulose is one of the most widely used carbohydrates to prepare bio-renewable resource based polymer nanocomposites. Raghavendra et al. [162] developed cellulose–silver nanocomposite fibres having wonderful antimicrobial properties from an eco-friendly process in which $AgNO_3$ had been reduced using gum acacia (GA) and guar gum (GG). The prepared nanocomposites had been characterized with spectral, and thermal, morphologic techniques. The data had indicated that AgNPs homogenously distributed in the cellulose matrix with strong interaction between cellulose and polymer/AgNPs. The cellulose-silver nanocomposite fibres (CSNCFs) had shown antibacterial activity against *E. coli*. Consequently, it was clearly understood that the AgNPs containing composite cellulose fibres could be utilized as an effective tissue scaffold for burn or wound healings. The fibres could be used for both long-lasting use as an antibacterial material in the textile industry and fabrics in surgical procedures (Figure 17).

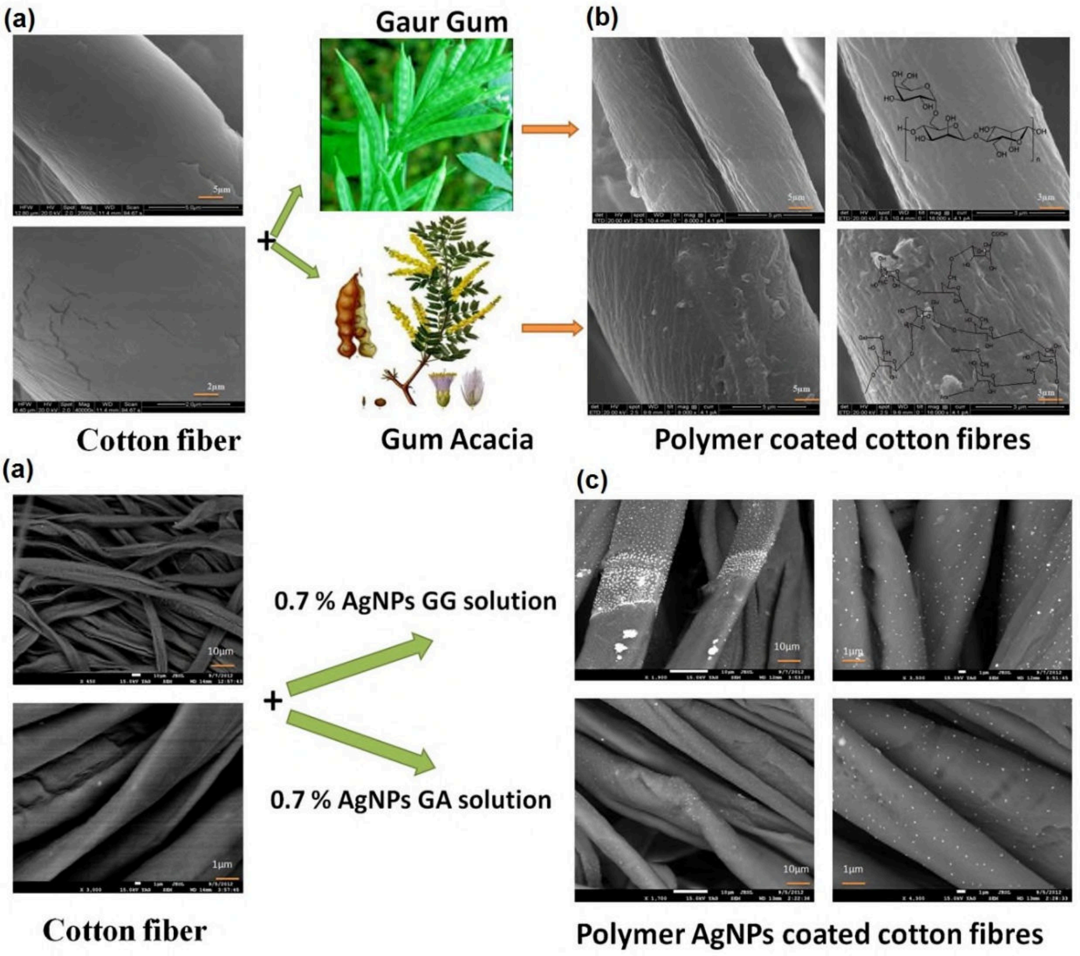


Figure 17. The SEM images of pure cotton fibres (a), polymer-coated cotton fibres (b), and polymer AgNPs coated cotton fibres (c). Reproduced with permission from ref [162]. Copyright 2013 Elsevier.

The nanocomposite for antibacterial purpose obtained from another polysaccharide had been used as a carrageenan matrix and composites had been prepared with the chitin nanofibrils (CNF). The prepared carrageenan/CNF nanocomposite films had been studied for their antimicrobial activities against *E. coli* and *L. monocytogenes*. Only carrageenan films showed no antimicrobial activity for both bacteria. Although carrageenan films including CNF had shown antimicrobial effect against *L. monocytogenes*, there had been no clear case for *E. coli*. Furthermore, the antimicrobial activity against *L. monocytogenes* had depended on CNF content. Although the total mechanism of antibacterial activity of CNF has not been explained so far, it has been believed that CNF makes bacterial clustering and inhibits growth depending on the mass transfer limitations resulted from the lack of oxygen and nutrients. [163] CH-nanocellulose films, in which both matrix and reinforcements are from bio-renewable resources, were prepared for the aim of antimicrobial property. It had been reported that since the thermal resistance was increased and CH-nanocellulose films could store food against both gram-positive like *S. aureus* and gram-negative such as *E. coli* and *S. enteritidis* bacteria for 6 days at room temperature. [164]

Essential oils are also being used in the nanocomposite based food protective films because of their strong antimicrobial character. In this context, alginate/clay containing a certain percentage of the essential oil films had been prepared. It had been found that these prepared films showed antimicrobial effects for 12 days against *S. aureus*, *E. coli*, and *L. monocytogenes* pathogens, which could widely reproduce in food. [165]

In another work, green tea (GT) based Ag^0 nanocomposite hydrogels were prepared successfully as an antibacterial hydrogel. The spherical Ag^0 nanoparticles were generated at the average size of 10 nm. The Ag^0 nanoparticles were developed by reducing of Ag^+ ions loaded hydrogel solution by ammonia gas. It was found that poly (green tea-acrylamide) P(GT-Am) hydrogel extremely stabilized the Ag^0 nanoparticles throughout the network of the hydrogel. These nanocomposite hydrogels were found to exhibit high significant antibacterial activity against *Escherichia coli* and *Staphylococcus aureus.* Therefore, these nanocomposites hydrogels have potential to be used for wound dressing and antimicrobial agent's applications. [166]

Recently, bacterial nanocellulose has been using in biomedical applications. Bacterial nanocellulose has taken more attention as a new wound dressing material. However, bacterial nanocellulose hasn't demonstrated any antimicrobial activity. Liyaskina et al. [167] had obtained bacterial nanocellulose with fusidic acid as an antibiotic. The bacterial nanocellulose was produced using *Gluconacetobacter sucrofermentans* (B-11267). The prepared biocomposites had demonstrated strong antibiotic activity against *Staphylococcus aureus* and have potential be utilized as a wound dressing material, especially in medicine.

Samples of antimicrobial applications of nanocomposites from bio-renewable resources are also given in Table 4 as summary information.

Table 4. Antimicrobial applications of nanocomposites from bio-renewable resources

Nanocomposite	Fabrication Techniques	Applications	Antimicrobial Activity Studies Against	Ref.
Cellulose–silver nanocomposite **fibre**s	The reduction of $AgNO_3$ using gum acacia (GA) and guar gum (GG)	Tissue scaffold for burn or wound healings	*E. coli*	162
Carrageenan/CNF nanocomposite films	Solution-casting technique	Food safety	*E. coli*, and *L. monocytogenes*	163
CH-nanocellulose films	Agitation and sonication	Food storage especially for the meat industry	*S. aureus*, *E. coli*, and *S. enteritidis*	164

Alginate/clay containing essential oil films	Addition of essential oil during the production procedure	Food protection as well as edible films	*E. coli*, *S. aureus*, and *L. monocytogenes*	165
Green tea (GT) based silver nanocomposite hydrogels	The reduction of Ag+ ions loaded hydrogel solution by ammonia gas	Wound dressing and antimicrobial materials	*S. aureus,* and *E. coli*	166
Bacterial nanocellulose with fusidic acid	A static culture medium by *Gluconacetobacter sucrofermentans* B-11267	Wound dressing material	*S. aureus*	167

3. Chemistry, Structure and Separation Applications of Nanocomposites from Bio-Renewable Resources

In today's technology, applications of the membrane are quite widely used in purification, enrichment of active ingredients, recycling of industrial byproducts and reducing the toxicity of wastes. Biocompatible nanocomposite membranes prepared from many renewable resources have been widely used in membrane technology. In these membranes, matrix structures which can particularly be adjusted in terms of pore size and distribution are preferred due to long-lasting usage.

3.1. Water Purification Applications

The porous and high polar structure of bio-renewable composites provides an important advantage for water purification applications. In particular, natural fibre-reinforced composites have significant potential in this field. Cellulosic plants and wood fibres, plant waste-based fibres and protein-derived fibres are the most preferred reinforcements. The strong interaction between polar groups and pollutants in these structures is the basis for good purification. Therefore, column fillers or membranes made of such bio-renewable reinforcement-based composites are frequently used in water purification processes.

Water resources have been exposed to intensive contamination by human activities such as agriculture, chemical, and material production, improper sanitation, manufacturing, electricity generation, mining and over the years. [168] Every year, the World Health Organization anticipates that more than 3.4 million people, especially children, die due to water-related diseases, and also 10% of diseases on the world can be prevented by developing the supply, management, hygiene and sanitation of water resources. [169] Therefore, shortage and pollution of global drinking water have increased the efforts in the area of developing highly effective water treatment methods. Recently, developments in engineering and nanotechnology show that many of the present problems concerned with the quality of water can be reduced by using nanocomposite-based treatment membranes. In particular, nanostructures having high adsorption efficiency, a large surface area and active groups that interact with contaminants have great potential in this area. [170,171] For the elimination of contaminants located in drinking water supplies methods such as membrane filtration, ion exchange, chemical precipitation, absorption and electrochemical are commonly used. Among these methods, membrane-based methods are widely used because of the advantages such as low energy consumption, using very low concentrations, high purification efficiency, simple operation, high selectivity, proper for green chemistry and lower operating costs. [172–174] Besides, the pore structure of the membrane to be used in this field can be easily adjusted by nanostructured reinforcements and whereby it is possible to remove different contaminants.

Membrane technology meets more than 53% of the production methods of freshwater in the world. [175] Due to the negative effects of contaminants such as insecticides, pesticides, heavy metals, paints, and industrial wastes on the environment and living beings the removal of these contaminants by membrane technology has become important. In particular, selective, polymeric membranes and polymer matrix nanocomposite membranes have become an important issue with their water separation performances. A significant ratio and speed of the use of membranes in the industrial field had also brought certain problems. The regeneration or destruction after using membranes has become a major problem. Therefore, the synthesis and use of membranes from natural and nontoxic components have been quite effective in solving these problems. In particular, nanocomposite membranes can be produced using natural or synthetic sources. Compared to natural polysaccharides or biopolymer-based nanocomposites, synthetic polymer-based nanocomposites have many properties such as better mechanical strength, higher chemical resistance, better stereospecific applications and longer life. However, since synthetic nanocomposites are not biodegradable, in particular, they lead to environmental pollution which is one of the biggest challenges in developed countries. Therefore, renewably sourced biopolymer-based nanocomposites are commonly used instead of synthetic polymers because of their unique characteristics such as low cost, non-toxicity, biodegradability and biocompatibility. [176] Such membranes are very useful for continuous use and are controlled with pore structures. In the research, Zirehpour et al. prepared composites including Boehmite (Bo) nanoparticles in cellulose acetate (CA) and cellulose triacetate matrix and had examined osmosis characteristics and water purification properties (Figure 18). [177]

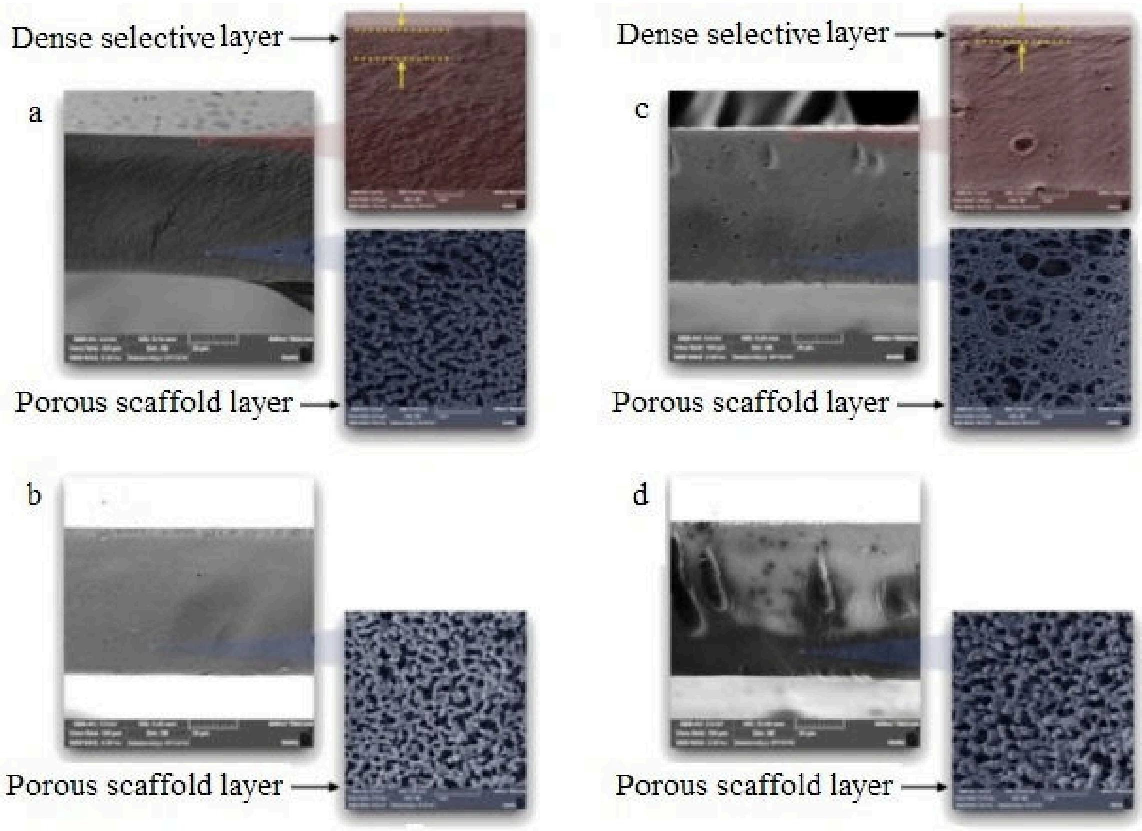


Figure 18. Field Emission Scanning Electron Microscopy (FESEM) micrographs of nanocomposites comprising of CA including Bo in different proportions (a) neat, (b) Bo-0.25, (c) Bo-0.5, and (d) Bo-1. Reproduced with permission from ref [177]. Copyright 2015 Elsevier.

Industrialization is the leading factor in the accumulation of toxic wastes containing many poisonous chemicals including heavy metals. Some of the most common heavy metals such as copper, chromium, lead, cadmium, nickel, mercury, and arsenic are released into the environment in dental applications and industries of tanning, textiles, electrolysis, metal salt production, paper and pulp. [178,179] As opposed to the traditional organics pollutants, heavy metals do not deteriorate and tend to get accumulated in living organisms particularly in the liver tissue. [180] The above-mentioned excessive accumulation of heavy metals damages the body's central nervous system, skin, dermatitis, and many systems. Therefore, bio-renewable resource-based nanocomposite membranes have been used for the elimination of heavy metals from water sources. Bio-renewable resources compared to synthetic polymeric membranes have many polar groups in their structures. Thus, they have a particularly important advantage in heavy metal binding. Therefore, protein, lignin and polysaccharides such as cellulose and chitin are widely utilized in nanocomposite membrane structures due to their cheap, renewable, environmentally friendly and biodegradability characteristics. [146,181,182] In particular, because they are insoluble and non-corrodible, these structures ensure advantageous properties in membrane applications. In this way, more resistant structures against the process pressure and deterioration can be obtained being used as a membrane.

Khan et al. [183] used anti-BC nanocomposites as a matrix for the assessment of wastewater (Figure 19). Nanocomposite structures had been synthesized by doping ZnO into the CA matrix. The authors anticipated that their synthesized nanocomposite structures could act as the membrane for removal of Mn^{2+}, Zn^{2+}, Pb^{2+}, Ni^{2+}, Cd^{2+}, Fe^{2+}, Al^{3+}, Sr^{3+}, and Sb^{3+} metals in the wastewater. The obtained results have also confirmed that cellulose acetate-ZnO nanocomposites could be used in the applications of water purification.

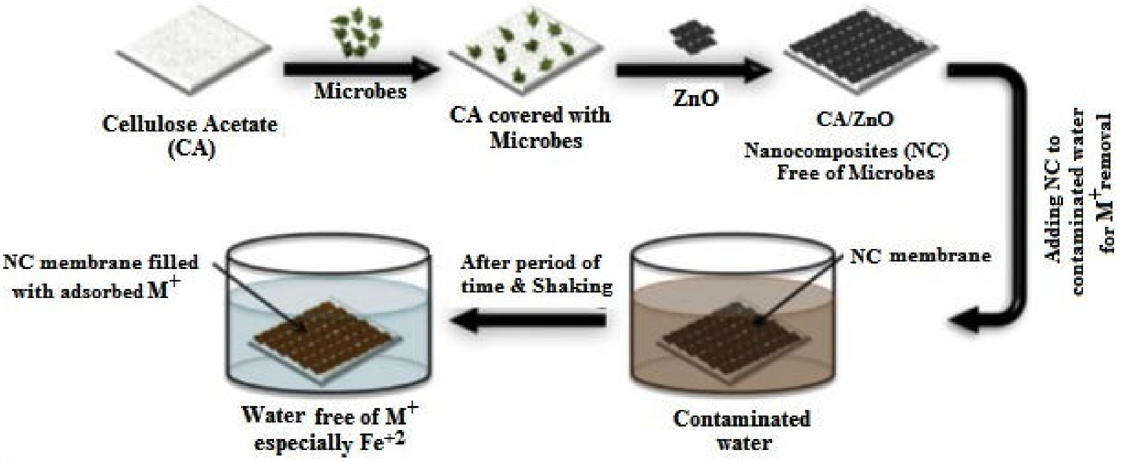


Figure 19. Schematic view of water treatment using nanocomposites. Reproduced with permission from ref [183]. Copyright 2015 Elsevier.

In a similar study, Badawi and his team [184] demonstrated that carbon nanotube-CA nanocomposites could be used in water purification as a membrane. Nevarez et al. [185] used biopolymer-based nanocomposite membranes in which lignin and cellulose triacetate were doped at different rates to remove fluoride, arsenic, calcium, sodium and magnesium elements from the wastewater. They had shown that such structures exhibit a high absorption capacity, especially in metal treatment.

It is well known that because of the chelating effect of the amide ends of CH in the glucosamine group, it adsorbs many heavy metal ions. Recent studies are having been focused on the removal of heavy metals by creating nanocomposites of CH nanoparticles with clay types such as bentonite, kaolinite, and montmorillonite. As chitin and CH, clays have a natural ability to remove heavy metals.

Bleiman and Michael [186] designed polymer-clay nanocomposites to absorb selenium from water. CH-montmorillonite nanocomposites showed the highest adsorption efficiency of selenium. In a similar study, Khedr et al. [187] suggested modified CH-montmorillonite nanocomposites to adsorb lead. Pandey et al. [188] used the CH-montmorillonite nanocomposites to remove the chromium metal from an aqueous solution. CH-coated bentonite nanocomposites had been used by Futalan et al. [189] to remove Cu (II) metals from an aqueous solution.

In a recent study, two new functionalized chitosan nanocomposites, (CH-Cinnamaldehyde (Cin) and Fe_3O_4@CH-Cin) were synthesized as adsorbent and used to remove toxic Cr (VI) from aqueous solution. The morphological, structural, and magnetic properties of composites were investigated. Toxic Cr (VI) adsorption mechanism was performed by batch experiments as a function of adsorbent dosage,_contact time pH, and initial hexavalent chromium concentration. At 298K, the CH-Cin adsorbent reached adsorption equilibrium within 35 minutes, while the Fe_3O_4® CH-Cin adsorbent reached adsorption equilibrium within 80 minutes. The maximum adsorption capacity for CH-C in adsorbent was 61.35 mg/g at pH=2, while the maximum adsorption capacity for Fe_3O_4@CH-Cin adsorbent was reported as 58.14 mg/g at pH=3. These results illustrated that two new functionalized nanocomposites will be promising candidate adsorbents for wastewater treatment applications [190].

Apart from CH and cellulose, to remove metals from wastewater, bio-renewable resourced nanocomposite structures have been fabricated as membranes by a number researcher. Chauke and his colleagues synthesized GO-α-CD-polypyrrole nanocomposites to remove Cr (VI) from aqueous solutions. [191] Polypyrrole has remarkable properties such as easy preparation, high chemical stability, cheap and ion exchangeability for removal of heavy metals. Therefore, Chauke et al. synthesized GO-α-CD-polypyrrole nanocomposites for removing Cr (VI) metal and determined the optimum conditions. In another work, Badruddoza et al. [192] produced Fe_3O_4 nanoparticles modified with carboxymethyl-β-CD (CM-β-CD) polymer for selective elimination of Ni^{2+}, Pb^{2+}, Cd^{2+}, ions from water. Due to having a loop structure, the CD is an important membrane matrix material for the transition metals having large radii such as Pb, Cd. Saad et al. prepared ZnO@CH core-shell nanocomposite by direct precipitation method (Figure 20). [193] They used the nanocomposites to remove Pb^{2+}, Cu^{2+}, and Cd^{2+} ions as adsorbent due to its inexpensive and low biological toxicity. The metal ions adsorption capacity values were determined as 117.6, 135.1, and 476.1 mg/g for Cu^{2+}, Cd^{2+}, Pb^{2+}, respectively.

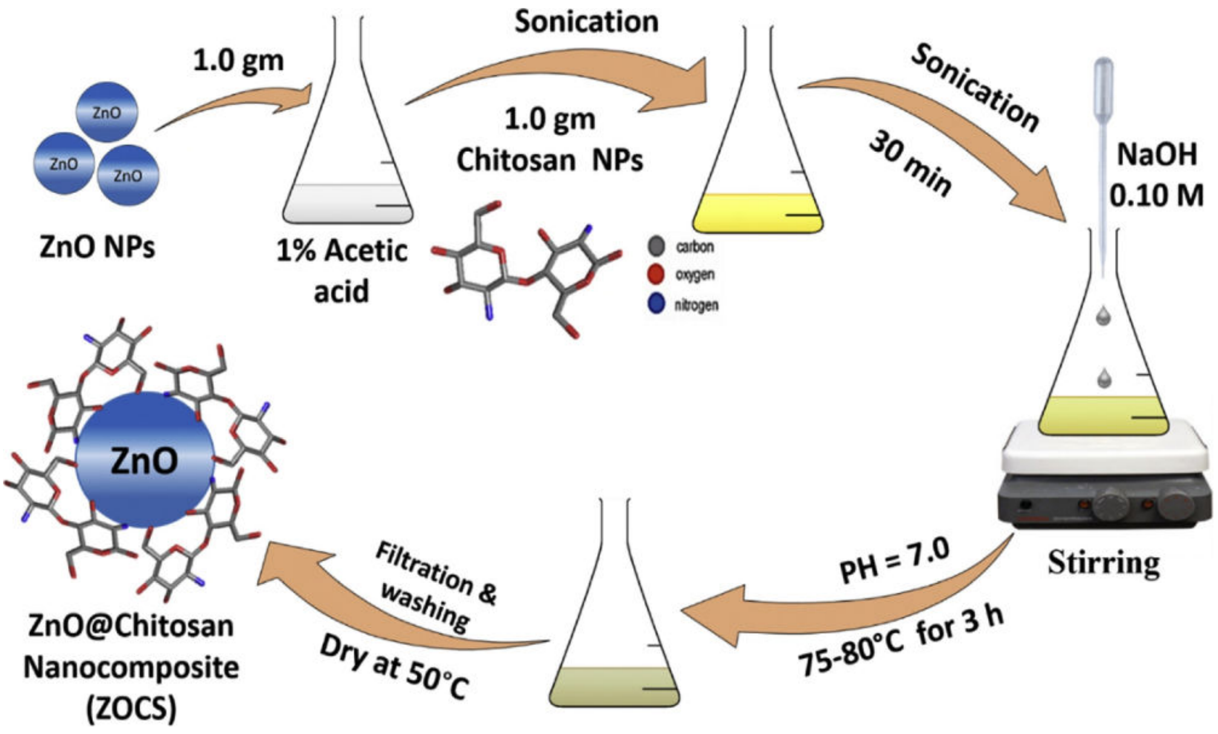


Figure 20. Synthesis of ZnO@CH nanocomposite. Reproduced with permission from ref [193]. Copyright 2018 Elsevier.

Bolisetty et al. [194] used amyloid–carbon hybrid membranes for the efficient purification of arsenic (both the arsenate (+5) and arsenite (+3))-contaminated water via a vacuum filtration technique. The amyloid fibrils were obtained from β-Lactoglobulin, which an economic milk protein (the key component of whey). Thanks to the suggested hybrid membrane, the As^{+5} and As^{+3} concentration decreased from 239 ppb to 3.3 ppb, and 258.3 ppb to 3.2 ppb, respectively. Also, the amyloid fibril adsorption capacity was approximately 7.4 and 18 times higher in comparison to the activated carbon for arsenate and arsenite adsorption, respectively. The authors reported that the prepared amyloid-carbon hybrid membranes can be reused for numerous cycles without any efficiency drop. The filtering efficiency was found to be 99.6% in real contaminated groundwater. Based on these results, the research team stated that amyloid-carbon hybrid membranes are a promising candidate for economic removal of arsenic from contaminated water.

In another study, amyloid fibril/ZrO_2 hybrid membranes were suggested for removal of fluoride (F^-) from wastewater and drinking water supplies.[195] These suggested amyloid fibril/ZrO_2 hybrid membranes exhibited an excellent performance such as superior selectivity, outstanding fluoride binding capacity, and fast purification to remove F^- by using filtration. Additionally, the authors highlighted that hybrid membranes have high potential to be applied for both low (several ppm) and high (even 200 ppm) levels to remove F^-.

3.1.1. Removal of Dyes

Recently, the removal of dyes and pigments from wastewater has become very important. The major one among organic and inorganic pollutants that contaminate water is organic dyes. These organic dyes are commonly used in many industrial areas such as plastic products production, tanning, food processing, papermaking, textile manufacturing, cosmetic preparation, and coating processes. It is hard to remove dyes from industrial wastewater and these dyes cause not only some toxic and carcinogenic effects on human health but also adverse effects on the environment. Therefore, when considering the potentials in environmental toxicity and damage to human health, renewably resourced nanocomposite membranes with different structures and reinforcements should be preferred to remove organic dyes from dirty water. [192] Carbohydrate type structures, which have strong interactions with dyes due to their polar groups, are very important in dye separation applications. Therefore, carbohydrate-based renewable composites have many applications in the field of dye removal and separation. Figure 28 shows the dyestuff structures in which cellulose fibres are used as a bio-renewable source in the removal processes of dyestuffs in wastewater. Strong secondary interactions between these structures and cellulose provide rapid and efficient treatments.

To eliminate cationic dyes from aqueous solutions Liu et al. [196] used β-CD/poly(acrylic acid)/GO nanocomposites as the membrane. They had used methylene blue and Safranin T as the cationic dye. Adsorption isotherm results showed that synthesized these nanocomposites kept more cationic dyes than other carbon-based adsorbents in the literature. Liu and his team had suggested that the new generation of β-CD/poly (acrylic acid)/GO nanocomposites would be an ideal material for removing dyes in wastewater. Carbohydrate-based bio-renewable resources are also used especially in the removal of anionic dyes. In another study with the anionic dyes such as reactive blue, Congo red and malachite green, Patra et al. [197] examined the dye removal properties of silica doped guar and gum nanocomposites. According to UV spectra obtained at different times, the absorption took place very quickly for reactive blue and Congo red dyes.

Wang et al. [198] used the magnetic β-CD/GO nanocomposites to remove malachite green from aqueous solutions. The results showed that the magnetic β-CD/GO nanocomposites have a promising adsorption ability to exclude dyes in water. Moreover, polyhydroxyethylmethacrylatemulti-walled carbon nanotubes (CH-MWCNT) nanocomposites were also used for the removal of methyl orange. [199]

Gomes et al. [200] reported that bio-renewable polysaccharide-based nanocomposites have the high potential to be used as membranes for the purification of wastewater (Figure 21). In their research, S/cellulose nano-hydrogel composite structures had been synthesized for adsorbing methylene blue which is a strong and effective dye. According to the obtained adsorption curves, the research group had reported that the S/cellulose nano-hydrogel composites had an effective ability to remove methylene blue from wastewater.

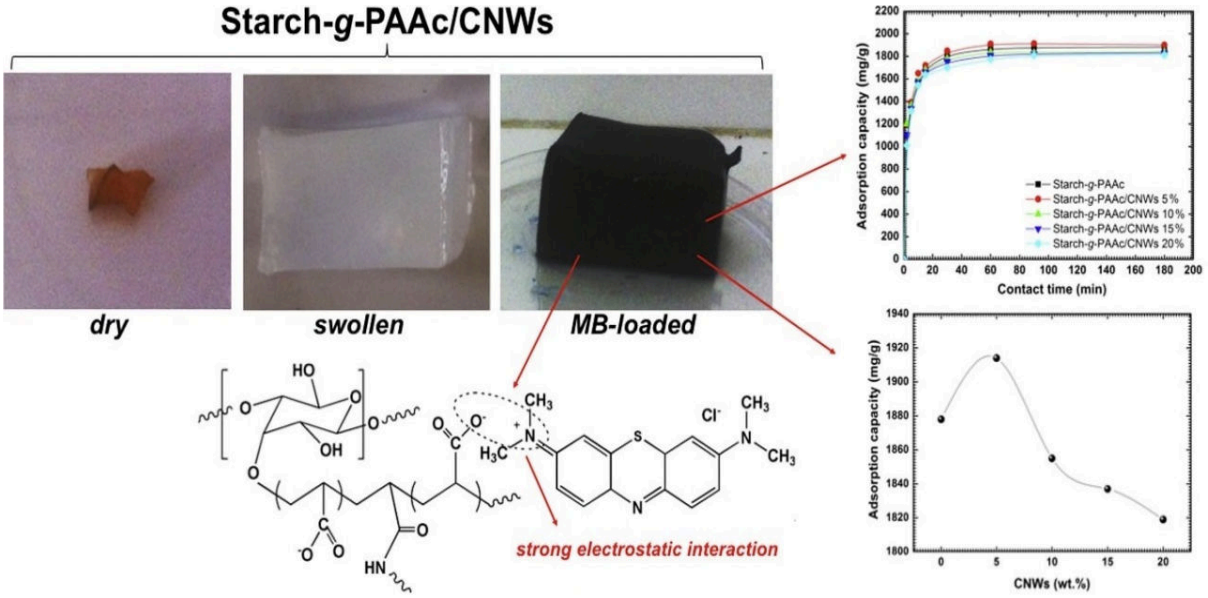


Figure 21. S/cellulose nano-hydrogel composite structures. Reproduced with permission from ref [200]. Copyright 2015 Elsevier.

Another nanocomposite structure that was completely formed from bio-renewable source had been reported by Karim et al. [201] The working team prepared a nanoporous membrane using cellulose nano nanocrystals functionalized with CH. The authors utilized the electrostatic attractive forces between cationic dyes (Rhodamine 6G, Methyl violet 2B and Victoria blue 2B) and negatively charged cellulose nanocrystals functionalized with CH to remove cationic dyes from water (Figure 22).

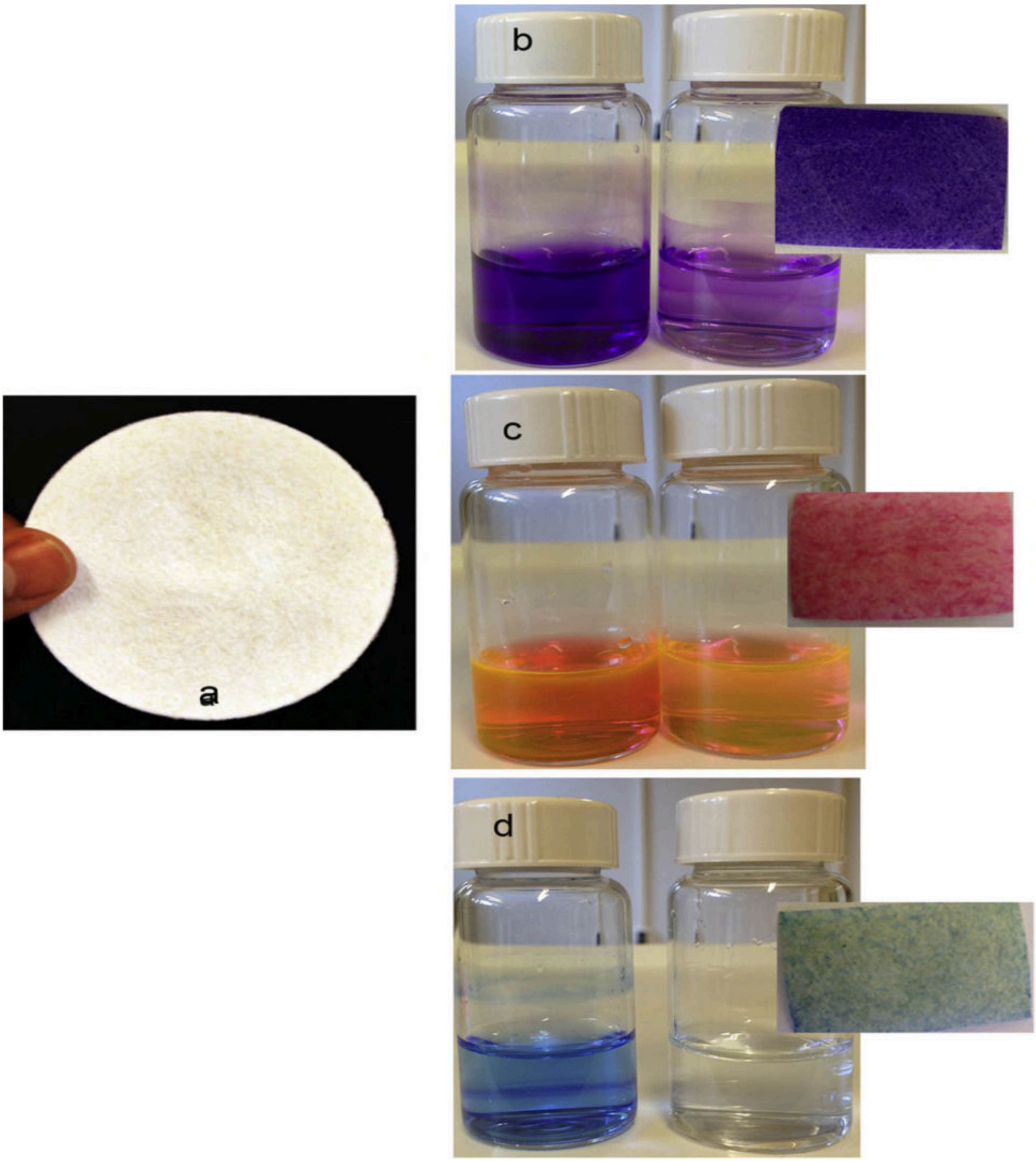


Figure 22. The removal efficiency of the cross-linked composite membrane. (a) Photograph of the membrane, water before and after adsorption test for (b) Methyl Violet, (c) Rhodamine 6G and (d) Victoria Blue. Reproduced with permission from ref [201]. Copyright 2014 Elsevier.

Sohni et al. developed CH/nano-lignin based composites as a novel adsorbent material to remove dye pollutant from aqueous solutions (Figure 23). [202] Under natural pH conditions, the fabricated novel material exhibited a high separation of 83% for methylene blue (MB) dye.

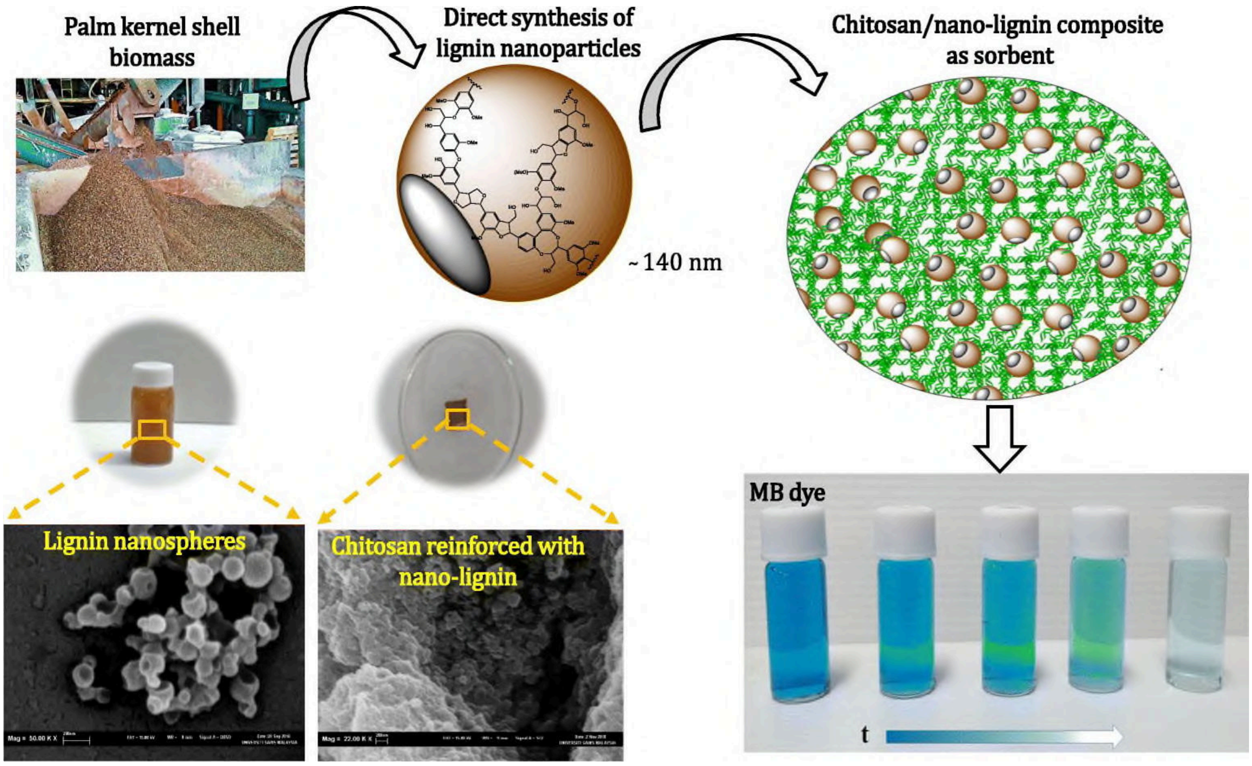


Figure 23. The preparation of developed CH/nano-lignin based composites and usage of to remove MB. Reproduced with permission from ref [202]. Copyright 2019 Elsevier.

In a recent study, CH/silica/ZnO hybrid nanocomposites were prepared by Hassan et al. [203] The prepared nanocomposites were characterized structurally, thermally, morphologically and were used to remove MB from wastewater. Furthermore, the effect of ZnO immobilization on the adsorption properties of nanocomposites was investigated in detail. According to the results obtained, the highest adsorption capacity of MB was reported as 293.3 mg/g in a slightly basic medium. The authors believe that these hybrid composites prepared for the adsorption of aqueous solutions of organic dyes have a promising future as an effective and cost-effective adsorbent.

In another recent study, H_2SO_4 cross-linked magnetic CH nanocomposite beads were prepared and applied as adsorbents for MB removal. Structural, morphological and crystallinity properties of H_2SO_4 cross-linked magnetic CH nanocomposite beads were studied in detail by various methods. Also, the effect of three different parameters on contact time, pH values and MB concentration on MB adsorption was investigated. According to the results, the equilibrium of H_2SO_4 cross-linked magnetic CH nanocomposite particles of MB adsorption was reached in 25 minutes of contact time. As the pH of the solution increased, so did the adsorption capacity. Based on the Langmuir isotherm model, the maximum adsorption capacity of H_2SO_4 cross-linked magnetic CH nanocomposite beads on MB adsorption was reported to be 20.408 mg/g. 204

3.1.2. Removal of Other Contaminants

Besides heavy metals and dyes, organic compounds used in the industry also contribute to the contamination of water. One of these is nitrobenzene, which is used in the production of products such as pesticides, explosives and dyes. [205] Wei and his team synthesized new HA-gelatin nanocomposites to remove nitrobenzene from aqueous solutions. [206] According to Langmuir and Freundlich adsorption curves, the maximum adsorption capacity was measured as 42.373 mg/g. These results indicate that bio-renewable based new HA-gelatin nanocomposites are effective adsorbents to remove nitrobenzene from aqueous solutions.

In another study in which renewable materials originated nanocomposites were used as a membrane, Suratago et al. [207] developed BC/alginate (BCA) nanocomposites in which BC was used as the main matrix to separate the ethanol-water mixture. In the study, BC hydrogels had been modified with sodium alginate. The BCA membranes showed the more hydrophilic property and pervaporation performance was found to increase.

3.2. Gas Purification Applications

Technological applications of gas separation have been increasingly developed to solve various global issues and challenges in recent years. Today, the widest industrial areas where these technologies are being used include [208]:

- Separation of nitrogen from the air
- Separation of water and CO_2 from natural gases
- Separation of hydrogen gas (for example, separation of H_2/hydrocarbon in petrochemical applications and separation of H_2/N_2 in nitrogenous plants)
- Separation of organic vapors from air or nitrogen streams

Since the separation process of the gas mixture is complicated and difficult, different separation methods have been developed such as membrane, adsorption, extractive distillation, and absorption. [209] Because of an economic and environmentally friendly technology, membrane-based gas separation techniques are the most commonly used methods. However, when conventional membrane materials are used, one of the most important barriers may be a case such as the increase of the selectivity and decrease of the permeability and vice versa. The development of hybrid or nanocomposite membranes to overcome this problem has been one of the most promising research direction in recent years.

Because nanocomposite membranes have some advantages such as control over porosity, good mechanical stability, and ease of processing, they are attractive as an alternative material compared to conventional separation methods. However, because of the ecological problems and the restriction of raw materials on the use of nanocomposite structured petroleum-derived polymers, researchers have headed towards the use of renewable and natural products in the development of nanocomposites. In technological industrial gas separation, cellulose is the most widely used renewable resource as a matrix material in nanocomposite membrane structures. CA and CNC had been tried successfully as the main matrix of the nanocomposite structure. Organic-inorganic nanocomposites are generally being prepared using zeolite, silica, alumina, carbon molecular sieve, etc. as additional reinforcements in polymer matrix because these materials increase the selectivity and permeability of nanocomposite hybrid membranes. Therefore, these inorganic reinforcements are usually supplemented up to the amount of 30-60%.

Two sections of the petrochemical industry are paraffin and olefins. Olefins have been used in the production of general plastics such as polypropylene and polyethylene as well as chemicals such as acetaldehyde, acrylic acid, acrylonitrile, ethylene oxide, and propylene oxide. One of the most significant and costly processes in the petrochemical industry is the separation of a mixture of olefins and paraffin. Today, the purification of olefins is performed by distillation. This process requires extremely much energy because of low bulk densities (1.09-1.15) of the components. Therefore, Naghsh et al. [209] used cellulose acetate-silicate nanocomposite membranes to separate the gas mixtures of ethylene/ethane and propylene/propane. The membranes were fabricated using the solution-casting method and characterized by SEM, FTIR and thermogravimetric analysis (TGA) methods. Besides, permeability and gas selectivity characteristics of the membranes were analyzed. Permeation experiments were conducted using a constant volume/variable pressure method under the pressure of 2 bar feed at 35°C. The obtained results had shown that when 30% of silica doped cellulose nanocomposites were used, the permeability of ethylene and propylene increased. Thanks to silica nanoparticles in the material, a physical barrier become against the path of gas diffusion and this barrier causes path long and winding. The diffusion coefficient and the resolution coefficient of prepared hybrid nanocomposite membrane had been indirectly determined using latency time (time lag method) and coefficients of permeability and diffusion, respectively. As a result of the study, the diffusion coefficient of gas decreased, and the solubility coefficient increased since the interaction between the cellulose chain and silica particles increased with the mass ratio augmentation of silica. The synthesized hybrid nanocomposites showed positive results in gas permeability and diffusion experiments Therefore, the use of cellulose-silica hybrid nanocomposites is precious in terms of separating olefin and paraffin mixtures.

In another study, Kim et al. had prepared nanoporous layered silicate/cellulose nanocomposite membranes to separate CO_2/CH_4 gas mixture. [210] For the gas permeation characteristics of CO_2 and CH_4, swollen silicate/CA composite membranes were investigated. The CA membrane's CO_2/CH_4 gas separation performance was importantly improved by combining 2–6 wt. % of swollen silicate flakes. A significant rise in CO_2 permeability was observed due to the preservation of selectivity. The present approach can prevent aggregation of particles and poor interfacial adhesion due to the excessive amount of inorganic filler.

3.3. Dye Purification Applications

Reactive dyes meet approximately 20-30% of the total paint market and interest on dyes is increasing every day since these dyes are widely utilized in several applications such as textiles, plastics, rubber, and leather tanning. [211–213] Inorganic salts and intermediate compounds which have low molecular weights along with other residues occur in synthetic processes. For improving the quality and purity of reactive dyes, the residual impurities and inorganic salts should be separated. The methods applied in conventional dye purification may cause high energy consumption, a low purification ratio, and severe environmental pollution. [214–216] Therefore, many innovative and green chemistry studies on the purification and decontamination of dyes from salts are still ongoing. Much of these works are about producing cheap, low energy consumption, environmentally friendly and bio-renewable materials. In this context, the most common method used for the purification of the organic dyes having a molecular weight of from 100 to 1000 Da is bio-renewable based nanocomposites membranes. In the literature, nanocomposite materials containing bio-renewable resources in the purification applications of dyes are limited. Therefore, the studies on such materials must be increased due to their advantages.

In the field of purification of dyes, clay/polymer hybrid nanocomposite materials have received a greater attraction due to their hydrophilic structure, high mechanical strength, and better thermal stability (Figure 24).

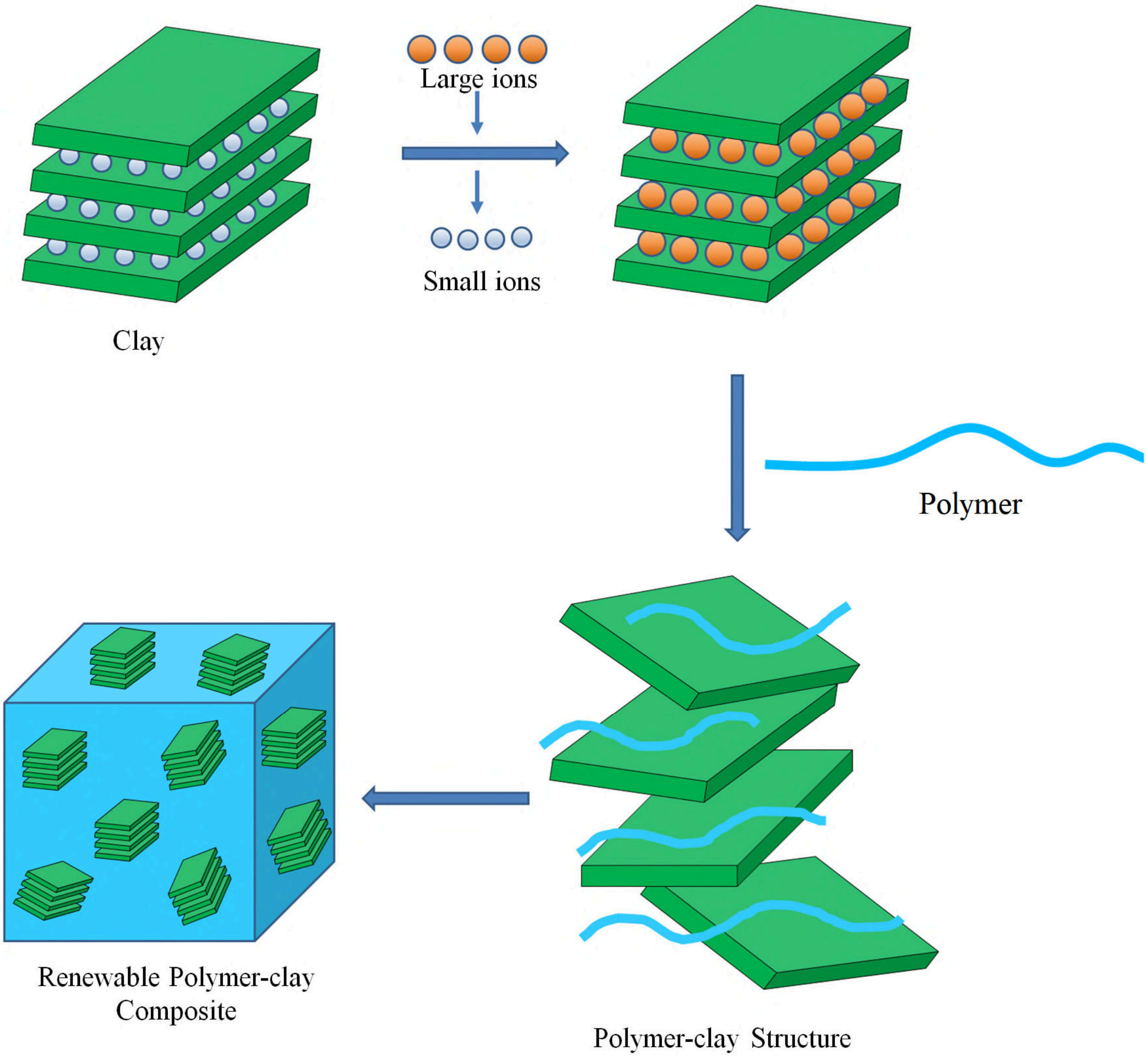


Figure 24. Preparation of clay/polymer hybrid nanocomposite materials.

Zhu et al. have prepared CH-MMT hybrid nanosheets with the phase inversion method for the applications in dye purification. [217] From these prepared materials, CH-MMT-polyether sulfone (PES) hybrid membranes were synthesized by doping of 0%, 0.5%, 0.75%, and 1% weight ratios. The synthesized membrane had been structurally and morphologically characterized by a variety of methods. After the addition of CH-MMT nanosheets, hydrophobicity and mechanical properties of hybrid membranes were found to be substantially improved. Also, the hybrid membranes had shown the antifouling property. More importantly, these prepared membranes, unlike traditional nanofiltration membranes, had shown low rejection for divalent salts, and high rejection for Reactive Black 5 and Reactive Red 49. Thus, membranes prepared by this method will be utilized for the purification of dyes in low pressure and high efficiency.

3.4. Other Membrane Applications

Besides the purification of water, dye and gas with nanocomposite membranes including bio-renewable resources (as matrix or reinforcement), different membrane applications such as the removal of phenolic compounds, the purification of alcohols like isopropanol, ethanol, methanol and the preparation of fuel cell membranes are also available in the literature.

Yang et al. [218] synthesized CdSe/BC nanocomposite membranes by *in situ* addition of CdSe nanoparticles to BC nanofibres (Figure 25). The study aimed to obtain luminescence nanocomposite membranes utilizing the optical property of CdSe quantum dots and biocompatibility, high crystallinity and mechanical properties of BC. Membranes prepared for this purpose were structurally, morphologically, thermally and mechanically examined. XRD patterns and FE-SEM images indicated that CdSe nanoparticles were evenly dispersed on the BC nanofibres. The thermostability of BC highly improved due to CdSe nanoparticles. The CdSe/BC nanocomposite showed good photoluminescence properties and better mechanical properties. The research team had reported that the study provided a simple method for the preparation of flexible BC membranes and the membranes can be used in advanced applications such as sensors, security papers, and flexible luminescent membranes.

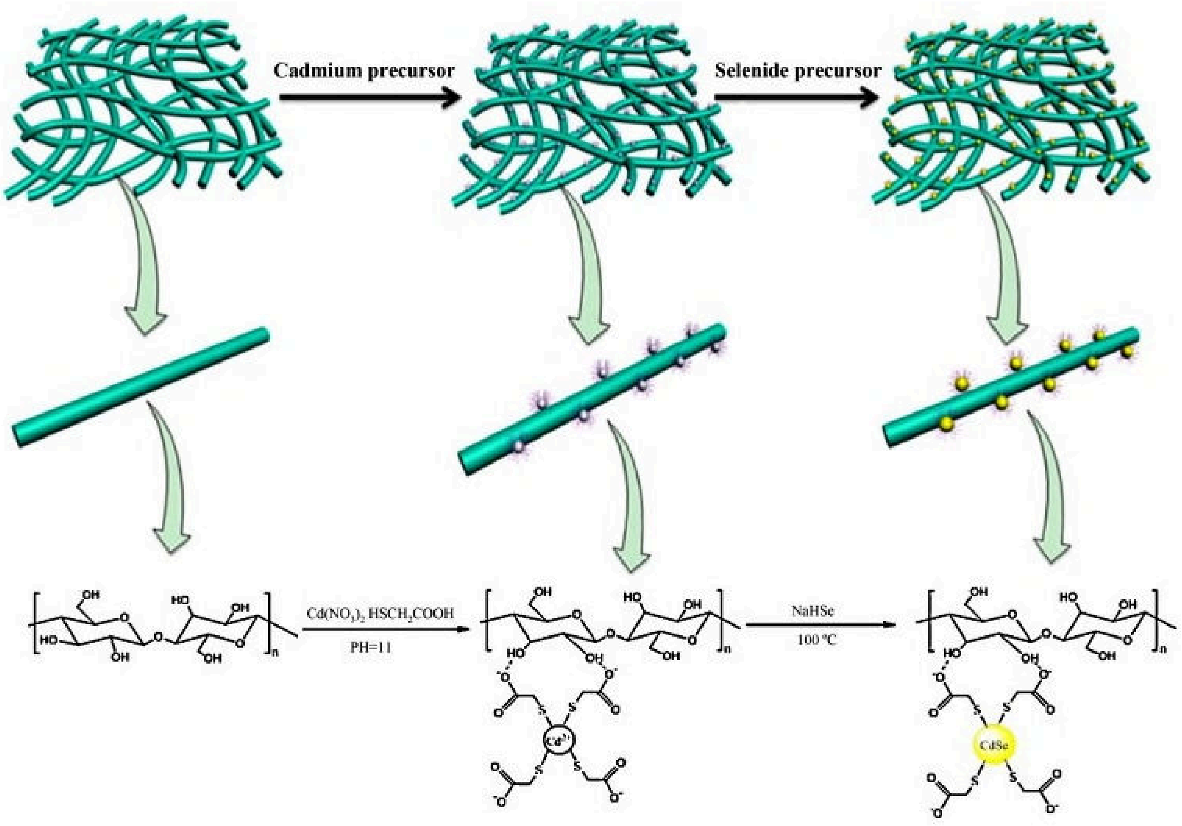


Figure 25. A schematic presentation of the preparation of CdSe/BC nanocomposites. Reproduced with permission from ref [218]. Copyright 2012 Elsevier.

Flexible BC/polyaniline (PANI) nanocomposite membranes had been prepared using oxidative polymerization of aniline with BC by Park et al. [219] The prepared membrane had been characterized by a different technique. BC had been developed using both mechanical properties and solvent stability of the BC/PANI nanocomposite membrane. Also, because of the presence of PANI, the nanocomposite membrane had increased electrical conductivity. As a result, the flexible membrane with high conductivity could be applicable for fuel cell barrier, electromagnetic shielding, chemical sensors and flexible display shortly.

In another study, the new conductive PANI/BC nanocomposite membranes were prepared by Hu et al. [220] The obtained results indicated that the prepared membrane exhibited high electrical conductivity (5.0×10^{-2} S/cm) and mechanical properties (Young's modulus was 5.6 GPa and tensile strength was 95.7 MPa). Furthermore, the electrical conductivity of the membrane was sensitive to the strain. The research group reported that prepared flexible films may be used in flexible electrodes, sensors, and flexible displays. Besides BC, CH is also widely used because of being easily modified, ease of isolation and mechanical properties in the membrane applications of nanocomposites. For instance, Yang and Wang [221] prepared novel graphene-modified polyvinyl alcohol/CH blend membranes or sulfonated graphene-modified polyvinyl alcohol/CH blend membranes. The ionic conductivity, thermal property, methanol permeability, and KOH uptakes of the PCG and PCsG nanocomposite membranes were determined. According to the obtained results, the research team reported that both nanocomposite membranes can be promising materials for future alkaline direct methanol fuel cell applications.

Ethanol and isopropanol should be of high-purity to be used in various applications, such as cosmetics, paints, adhesives, pharmaceuticals, coatings, and cleaning agents in the semiconductor industries. However, they form azeotropes at little water concentrations and are miscible with water. [222] Following this purpose, Dharupaneedi et al. [222] fabricated modified graphene/CH nanocomposite membranes to dehydrate ethanol and isopropanol. The prepared membranes were analyzed via contact angle, SEM, XRD, and optical profilometry methods. Compared to the ethanol-water mixture, the nanocomposite membranes indicated high separation efficiency for the isopropanol−water mixture.

Samples of separation applications of nanocomposites from bio-renewable resources are also given in Table 5 as summary information.

4. Chemistry, Structure and Electronic Applications of Nanocomposites from Bio-Renewable Resources

Today's technology is continually minimizing dimensionally, being accelerated and evolving to keep up with the pace of modern human life. This change in technology directly affects both chemistry and materials science and is forced to develop making our lives more active and efficient than we currently have right now. The development and the production of innovative materials that can particularly have multifunctional properties have become an important expectation. Use of multifunctional and smart technologies in electronics, medical, defense and automotive industry is an indispensable requirement today. Since the electronics industry is indispensable for modern human beings, advanced material designs are needed in this area. Sensors, capacitors, resistors and magnetic materials are constantly being developed. A continuous increase in the number of used products and unemployed devices in this area causes several environmental problems. Increased demand requires continuous production and bio-renewable resources are capable of responding to this request. In another aspect, this very fast technology change leaves an unemployed stack. Therefore, many types of researches are ongoing in the recycling of electronic waste today. The use of bio-renewable eco-friendly materials in the electronics industry will end the problem of electronic waste. Nanocomposites obtained from bio-renewable resources have been also used in the production of sensors, energy storage units, coatings, circuit components, and optoelectronic materials.

4.1. Chemistry, Structure, and Sensing Applications

Due to the serious problems related to the use and production of energy, the bio-renewable energy sector has begun to develop and use nanotechnology applications. Because of the advantages like adjustable porosity, high thermal and chemical stability, high selectivity and easy design, nanocomposites and hybrid nanocomposite are widely being used as ideal materials in various sensor technology (metal, gas, humidity, pressure, biomolecules, etc.). [223]

In sensor applications, bio-renewable resources are used such as chitin, CH, cellulose, CD, alginate, and guar, in particular. Figure 26 shows the preparation of a sensor for nanocomposites obtained from bio-renewable resources.

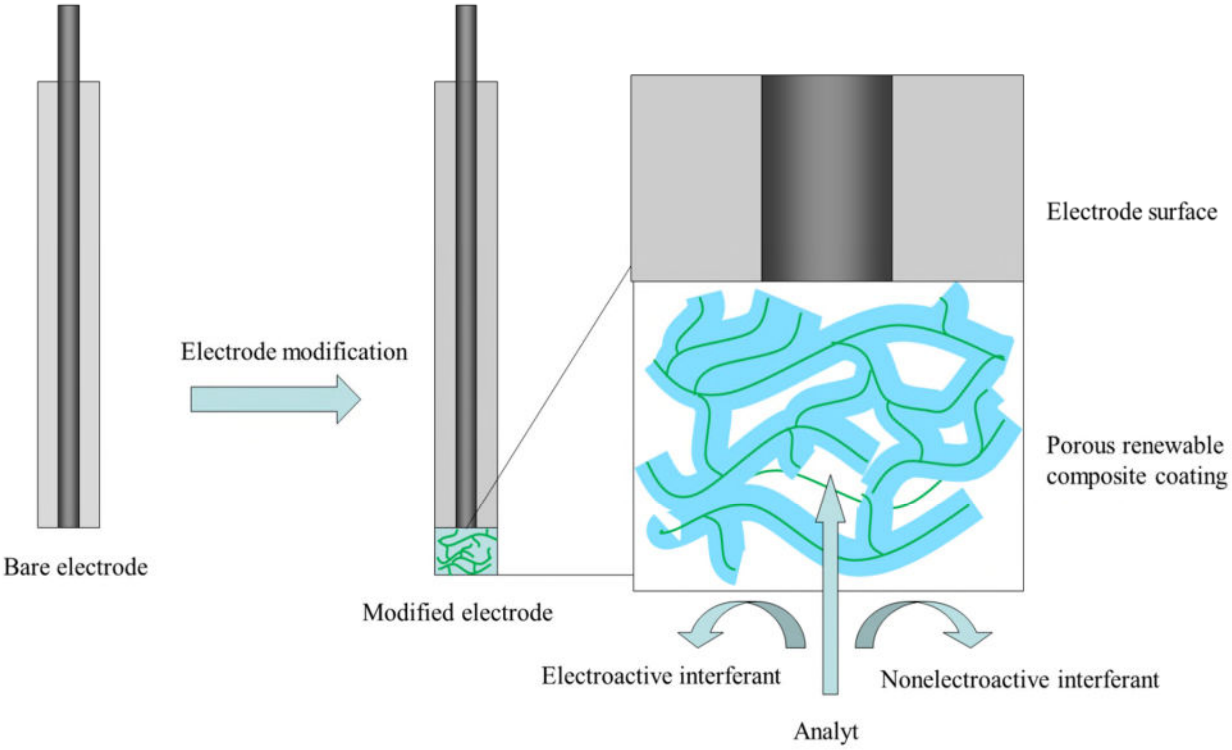


Figure 26. Schematic preparation steps of the sensor from bio-renewable sources.

Table 5. Separation applications of nanocomposites from bio-renewable resources

Composite	**Contaminants**	**Adsorption capacity**	**Ref.**
CA-ZnO	Fe (II)	7549.123 mL/g	183
CH-Cin	Cr (VI)	61.35 mg/g	190
Fe_3O_4@CH-Cin		58.14 mg/g	
CH–Montmorillonite	Se	18.4 mg/g	186
CH-Nanoclay (Cloisite 10A)	Cr (VI)	357.14 mg/g	188
CH-Bentonite	Cu (II)	14.92 mg/g	189
CH-Montmorillonite	Pb (II)	92 mg/g	187
GO-αCD-PPy	Cr (VI)	606.06 mg/g	191
CM-β-CD/Fe_3O_4	Pb (II), Cd (II), and Ni (II)	64.5, 27.7 and 13.2 mg/g	192
ZnO@CH	Pb (II), Cd (II) and Cu (II)	476.1, 135.1 and 117.6 mg/g	193
β-CD/PAA/GO	MB and ST	247.99 mg/g and 175.49 mg/g	196
Guar gum/SiO_2	RB and CR	-	197

Fe_3O_4/β-CD/GO	Malachite green	740.74 mg/g	198
pHEMA–CH-f-MWCNT	Methyl orange	306 mg/g	199
Starch-g-PAAc/CNWs	MB	~2050 mg/g	200
CNC/CH	Methyl Violet 2B, Victoria Blue 2B, and Rhodamine 6G,	-	201
CH/nano-lignin	MB	74.07 mg/g	202
CH/silica/ZnO_2	MB	293.3 mg/g	203
CH/Fe_3O_4	MB	20.408 mg/g	224
HAP–GEL	Nitrobenzene	42.373 mg/g	206
Amyloid–carbon	As (V) and As (III)	0.266 µg/mg and 1.133 µg/mg	194

4.1.1. Biosensor Applications of Chitosan-Based Nanocomposites

CH is widely used in sensor applications after being modified with metal oxide compounds because of some properties such as ease of film formation, high mechanical strength, biocompatibility, high water permeability, the susceptibility of chemical modifications and inexpensive. [225] The metal oxide nanoparticles exhibit some unique features such as having high catalytic activity, strong adsorption properties, large surface area and high surface to volume ratio. Metal oxides such as SnO_2 [226], ZnO_2 [227], TiO_2 [228], ZrO_2 [229] and CeO_2 [230] have been used as possible materials in biosensor applications. In particular, in the production of glucose sensors without enzyme and H_2O_2 sensors metal oxides have significant potential. In keeping such metal oxides on the surface of the electrode, bio-renewable saccharide-based polymers have been used as a matrix. In these structures, a strong interaction among -OH groups of the metal oxides surfaces and -OH groups of the matrix structure occur and therefore, the surface adsorption of metal oxides increases. [231]

Malhotra et al. [225] developed a cholesterol biosensor by synthesizing cerium oxide (CeO_2)/CH nanocomposites on indium-tin-oxide. Cholesterol sensors which have high selectivity and are easily designed are needed since the determination of cholesterol level is important for the diagnosis of coronary heart diseases. [232] CeO_2 nanostructures are known for many advantages such as being processed at low temperatures, being adjusted of the physical parameters, optically transparent, inert and thermal stability. [225]

In the context of work, CeO_2 nanoparticles had been successfully doped into the CH matrix and cholesterol oxidase (ChOx) had been immobilized to these nanocomposite structures for cholesterol determination. During this immobilization, the structure and the functional groups of the CH molecule increase the adsorption of the enzyme but do not inhibit the activity. In this system since CeO_2 increases the electroactivity on the surface, it accelerates electron transfer and thus shortens the response time. Furthermore, because of the porous and cavital structure of the electrode surface, the prepared sensor had been less sensitive to the concentration of the analytes. Therefore, the detection ranges of CH-Nano-CeO_2/ITO sensors as 10-400 mg/dL had been determined. The response time and detection limit of the CeO_2 nanoparticle-based sensor were found 10 s and 5 mg/dL, respectively. Km value as 3.5 mg/dL and regression coefficient value as 0.994 has also been seen.

Yu et al. [233] developed an electrochemical CH-Fe_3O_4 nanocomposite sensor for the recognition of Bisphenol A (BPA) as amperometric. BPA, especially today, plays an active role in the production of substances such as plastic, nylon, polyester and polyvinyl chloride. The polycarbonate is used as a coating material in plastics and inside of the food packages such as cans and juice boxes. In our daily lives, BPA appears much more in water bottles, containers, bottles, and glasses. The food contamination of bisphenol A which has carcinogenic effects is dangerous to our health. Also, BPA is assumed to cause sperm disorders and birth defects and cause various types of cancer, such as prostate, testicular and breast cancer. [234] Thus, the improvement for practical, effective and accurate electrochemical sensors to detect BPA has become an important issue. In this study, the quantity of CH–Fe_3O_4, deposition potential, measurement time and the pH effect had been optimized. Oxidation peak current had been commensurate with Bisphenol A concentration between 5.0×10^{-8} mol/dm^3 and 3.0×10^{-5} mol/dm^3. The detection limit of the electrode and the correlation coefficient had been determined as 8.0×10^{-9} mol/dm^3 and 0.9992, respectively. The prepared sensor had been successfully used to determine BPA. The study team had reported that this method is more suitable for practical electrochemical determination of BPA in industrial applications.

In a recent work [235], self-assembled graphene nanoplatelets (GNPs)-MWCNT-CH nanostructures were suggested for selective and highly-sensitive determination of BPA in milk samples. The GNPs-MWCNTs-CH composite was characterized concerning interaction, morphology, surface composition, surface charge and stability. Afterwards, the electrochemical performance of the GNPs-MWCNTs-CH composite modified sensor was studied. The linear response range under optimum conditions, for QR, was found to be from 0.1 to 100 µM with a low detection limit of 0.05 nM. In the meantime, the suggested modified sensor exhibited high resistance to interference, good repeatability and excellent reproducibility.

Nivethaa et al. [236] synthesized polymer matrix based CH-Ag nanocomposites containing silver in various proportions of weight %. The study aimed to show that CH-Ag nanocomposites, whose matrix is an edible biopolymer, could be used as mercury (Hg) sensor. Hg is an important and toxic heavy metal on the earth. Hg (II) is highly reactive, toxic, and the most common form of mercury. [237] It is required that the amount of mercury in water has to be known because it damages the endocrine system of the brain and kidneys. Therefore, various methods and techniques for the removal of Hg^{2+} ions from water and wastewater have been investigated. From some different sensor applications, colorimetric sensors depending on the colour change by the addition of mercury have attracted much attention because they not only have a simple technique but also give economical and reliable results. [234] AgNPs have many applications such as antibacterial activity, the determination of various ions, the inhibition of HIV-like diseases and tumors and the determination of pH and glucose. However, the increase in the particle size of silver occurs as a major problem because of its disadvantage related to the accumulation. As a consequence, the binding of silver particles to the receptor is more difficult and the specificity decreases. [238] A surfactant and CH, which gains some features to a composite such as biocompatibility and biodegradability, eliminate the harmful effects of nanoparticles. The presence of AgNPs in the CH matrix synthesized as the nanocomposite structure had been displayed by the working team with TEM (Figure 27). Moreover, the bonding of NH_2 and OH groups, which CH have, with silver had been proved by FTIR and XPS measurement techniques. The absorbance increase in the results of UV-Vis analysis had confirmed that the amount of silver in the nanocomposite structure increased. Face centered cubic structure of silver and semi-crystalline property of CH had been determined by XRD analysis. The interaction of nanocomposite material which was used as a colorimetric sensor to detect mercury had been confirmed by a decrease in the intensity of UV-Vis measurements. The detection limit had been found as approximately 7.2×10^{-8} M. According to the obtained results, Nivethaa et al. reported that nanocomposites containing high selective, non-toxic and environmentally friendly bio-renewable resources are ideal materials for the determination of mercury in low concentrations.

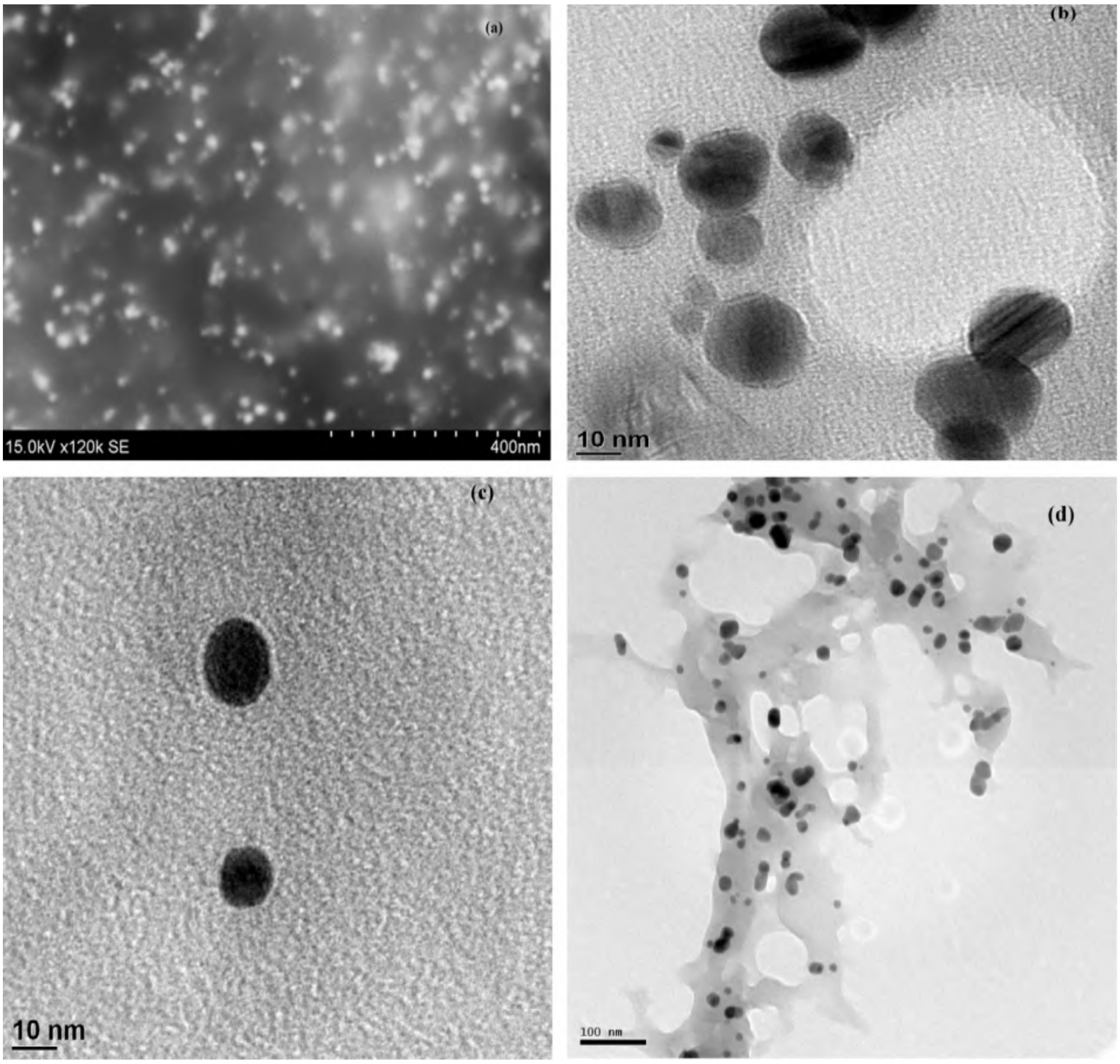


Figure 27. FE-SEM image (a) and HRTEM images (b, c, d) of CH–Ag nanoparticles. Reproduced with permission from ref [236]. Copyright 2015 Elsevier.

In a recent study, Sadani et al. suggested CH-gold nanoparticles based optical sensor on bovine serum albumin (BSA) for detection of low concentration of Hg (II) ion in different samples such as water, soil, and food samples. [239] Figure 28 depicts the schematic fabrication procedure of the sensor. The developed optic **fibre** sensor can detect Hg (II) ion in different water, soil and food samples with a LOD of 0.1 ppb. Besides, it was highly stable and repeatable and this sensor measures with a handheld reader previously reported.

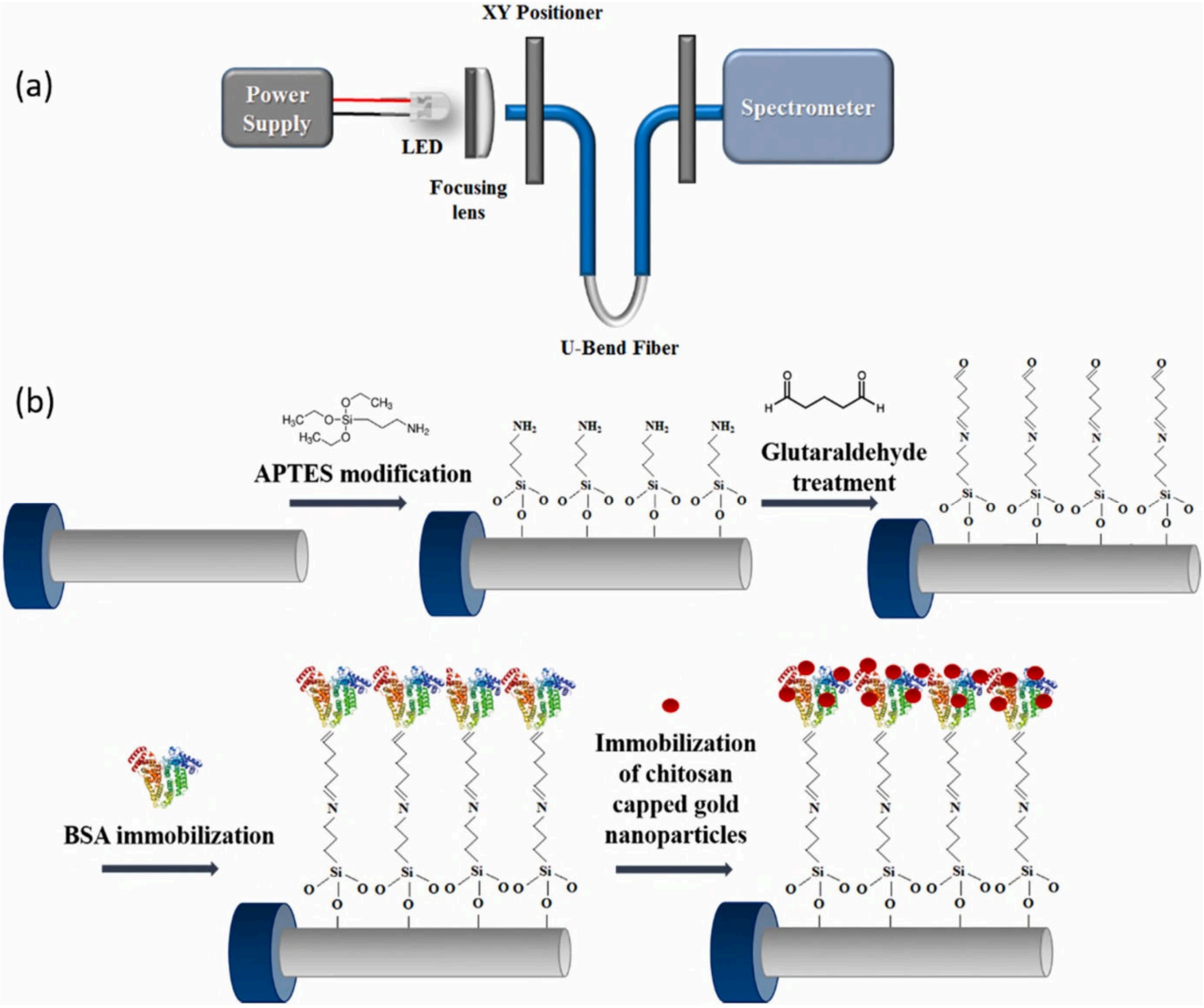


Figure 28. (a) The general structure of CH - gold nanoparticles based optical sensor (b) preparation of the sensor (i) amine functionalization using (3-Aminopropyl) triethoxysilane (APTES) (ii) glutaraldehyde treatment (iii) immobilization of the BSA on glutaraldehyde (iv) immobilization of CH capped gold nanoparticles on BSA. Reproduced with permission from ref [239]. Copyright 2019 Elsevier.

Chromium (Cr), which is as toxic as mercury, is another heavy metal that is extensively used in diverse industries such as metallurgy, metal melting, coating and electroplating industry, rechargeable battery industry, pigment production, wood preservation, and free tanning. [240,241] It is a form of Cr (III) and Cr (IV) having some physicochemical properties and toxicities as heavy metal. [242,243] Cr (III) is recognized as a necessary nutritional element for living organisms. Besides, it is an indispensable element in mammals and has an effective role in carbohydrate, lipid, glucose and protein metabolisms. [244] Both lack and excess of this element lead to negative effects on the human body. For this reason, some important techniques such as AAS, AES, inductively coupled plasma mass spectrometry (ICP-MS), chemiluminescent, fluorescence resonance energy transfer assay, colorimetric, hyper Rayleigh scattering, fluorescent and spectrometric analysis have been established for the detection of Cr (III) in industrial and biological samples. However, most of these methods are expensive, take much time, tedious in terms of sample preparation and required special equipment. Thus, for the determination of Cr (III), highly efficient in terms of electrochemical oxidation, versatile, easily manipulated, environmentally friendly and cheap alternative methods have been investigated. Today, nanotechnology science has begun using new nanomaterials to produce chemically modified electrodes. In this regard, bio-renewable natural products and metal oxides have the most ideal structures. Salimi et al. [245] prepared a novel electrochemical Cr (III) sensor. In their study, the manganese oxide (MnO_x)/MWCNTs/CH nanocomposites had been prepared. MnOx has excellent nanostructure and is a suitable candidate as an electrode material having advantages such as low cost, non-toxic, natural wealthy, environmentally friendly and relatively high energy density. Therefore, it is being widely used as biosensors/ chemical sensors. In the study, primarily glassy carbon electrode (GCE) was modified with CH/MWCNTs nanocomposite thin films. Then, MnOx nanostructures were immobilized onto the surface of CH/MWCNTs modified glassy carbon electrode with a combination of constant potential (0.6

V) and cyclic voltammetry (0.3-0.6 V) measurement techniques. Prepared MnO_2 based electrode had shown a good pair of redox for the $Mn^{2+/}MnO_2$ system. The charge transfer coefficient, the constant of electron transfer rate and surface concentration had been measured as 0.394, 3.44 s^{-1}, $3.3x10^{-11}$ mol cm^{-2}, respectively. Modified electrode had shown high electrocatalytic activity toward the oxidation of Cr (III) in neutral pH. Cyclic voltammetry and hydrodynamic amperometric methods had been used to determine chromium. The detection limit, the selectivity and linear concentration range of the prepared sensor had been measured as 0.3 µM, 18.7 nA μM^{-1} and from 3 µM to 200 µM. In addition, the sensor had remained 90% of its authenticity after even being waited 3 months in favorable conditions. As a result, it had been seen that CH, which was in the structure of the synthesized nanocomposite material for the detection of Cr (III), played an important role in especially binding of reinforcement and extending the shelf life of the sensor.

Phenols and simple phenol-derived phenolic compounds are extensively used in several industries such as polymeric material industry, pesticides, dye industry, petrochemical products, and wood preservatives. [246] Many of these compounds are in the water, food, and drugs. They are extremely harmful to human health when inhaled or taken by mouth and skin. [247] Therefore, due to the persistence in environment and toxicity, it is extremely important to develop simple techniques for the rapid measurement of phenolic compounds. Chromatographic and spectrophotometric measurement techniques have been used to detect phenolic compounds in water samples, However, these measurement techniques are expensive, time-consuming, limited and complicated in terms of the implementation. Electrochemical biosensors are considered to be promising due to the high selectivity, the fast and simple implementation for the determination of phenolic compounds. Therefore, Han et al. [248] tried to develop a highly selective and simple amperometric biosensor for phenols. In this context, using CH as a bio-renewable resource, CdS quantum dots/CH nanocomposite structure had been prepared and tyrosinase had been immobilized into the nanocomposite matrix to be used as a biosensor for the determination of catechol. CH had incorporated biocompatibility and hydrophilic characters to the nanocomposite structure. Moreover, the structure of the CH had increased the absorbed analytes compounds on the electrode surface and thereby increased the effectiveness of the sensor. It had been observed that the activity of the tyrosinase enzyme, which was immobilized onto the new nanocomposite structure, had been largely preserved. CdS quantum dots/CH nanocomposite films had been characterized by SEM and electrochemical impedance spectroscopy. Also, biosensor parameters had been optimized with a variety of experiments. Under optimum conditions, the proposed biosensor had given a response in the range of 1.0×10^{-9} - 2.0×10^{-5} M catechol concentration and the selectivity and the detection limit had been measured as 561 ± 9.7 mA M^{-1} and 0.3 nM (signal-to-noise ratio of 3), respectively. Han et al. showed that for the determination of phenolic compounds and the development of biomatrix and biocatalysts in nanotechnology, CdS quantum dots/CH nanocomposites could be used. Besides, Carlo et al. used gold-CH nanocomposite material for the determination of caffeic acid. [249] Caffeic acid is a recently explored interesting antioxidant because of its pharmacological properties and benefits to human health. Therefore, a rapid and simple determination of caffeic acid is important with electrochemical sensors. In recent years, AuNPs have shown unique physical and chemical properties and these nanoparticles have been increasingly used in some important industrial applications such as electronics, biotechnology, medical, optics, biomaterial, and catalysis. Nanocomposite structured CH and AuNPs had been used for the sensing of caffeic acid. In this study, colloidal AuNPs had been immobilized into the CH matrix using the green chemistry method. In the aqueous solution of CH and some organic acids (acetic, ascorbic, malonic or oxalic acid, etc.) the reduction of Au^{III} to Au^0 had been provided with a synthesis reaction performed in situ. CH, which is biocompatible and a bio-renewable resource through having amino and hydroxyl groups, provides a simultaneous synthesis and surface modification of gold nanoparticles. Hybrid nanocomposite films of AuNPs-CH had been obtained with the good film ability of CH. Au-CH nanocomposites were successfully used as selective and sensitive electrochemical sensors for the determination of caffeic acid. Limit of detection and concentration range had been measured as 2.50×10^{-8} M and from 5.00×10^{-8} M to 2.00×10^{-3} M, respectively. Carlo et al. reported that the new green synthesis method used in the study and the high performance of Au-CH hybrid nanocomposites would give a direction to the new approaches.

Yang et al. [250] developed an impedimetric electrochemical DNA sensor. MWNTs-CH-SnO_2 hybrid nanocomposites had been synthesized to be used as a biosensor. CH had been used in the nanocomposite structure because of its properties related to biodegradability and biocompatibility. Inorganic oxides are widely used to improve the transfer of electrons between the electrodes and biomolecules. Due to the advantages such as outstanding photo electronic features, short response time, high selectivity and conductivity, SnO_2 are used in microelectronic, photonic, solar cell and biosensor applications. Therefore, SnO_2 had been preferred as the inorganic oxide compound in the study. Yang et al. characterized the Au electrode modifying with MWNTs-CH-SnO_2 composite with electrochemical impedance spectroscopy and cyclic voltammetry. This prepared nanocomposite structure demonstrated the most significant electrochemical signal compared to MWNTs-CH, SnO_2-CH, and bare gold electrode. The electrochemical DNA had been used to determine the phosphinothricin-acetyl-transferase gene in transgenic maize. The detection limit and the dynamic detection range had been measured as 2.5×10^{-12} M, and from 1.0×10^{-11} to 1.0×10^{-6} M. As a result, based on the performed research, it had been demonstrated that this designed biosensor has unique advantages such as simplicity, stability, and high selectivity.

Baccarin et al. showed the simultaneous electrochemical detection of paracetamol (PAR) and dopamine (DA) amount in urine samples using reduced graphene oxide(rGO)/carbon black(CB)/CH composite modified GCE (Figure 29).[251] This electrochemical sensor showed good analytical performance for DA with a wide concentration range from 3.2×10^{-6} to 3.2×10^{-5} M. This modified electrode also showed a low detection limit (2.0×10^{-7} M). For PAR, the prepared sensor displayed a wide concentration range from 2.8×10^{-6} to 1.9×10^{-5} M and a detection limit of this sensor was 5.3×10^{-8} M. This sensor was not affected by other interfering species during urine measurements. The developed sensor can be a promising biosensor candidate because of the advantages such as low cost, easy preparation, selective and fast response. Therefore, it may be used to detect paracetamol and dopamine in some biological models. Thus, this sensor can be used for many biomedical applications.

In the literature, there have been many reports including CH-based hybrid nanocomposite for the preparation of a glucose biosensor. Figiela et al. [252] fabricated a non-enzymatic glucose biosensor with the help of copper oxide-CH nanocomposites by a biomimetic approach (Figure 30). The sensor showed suitable analytical performances with good sensitivity (503 μA.mM/cm^2) in a wide linear range, low detection limit (11 μM) and very short response time (within 6 s). Furthermore, the novel sensor can be suitable for the detection of glucose in biological fluids.

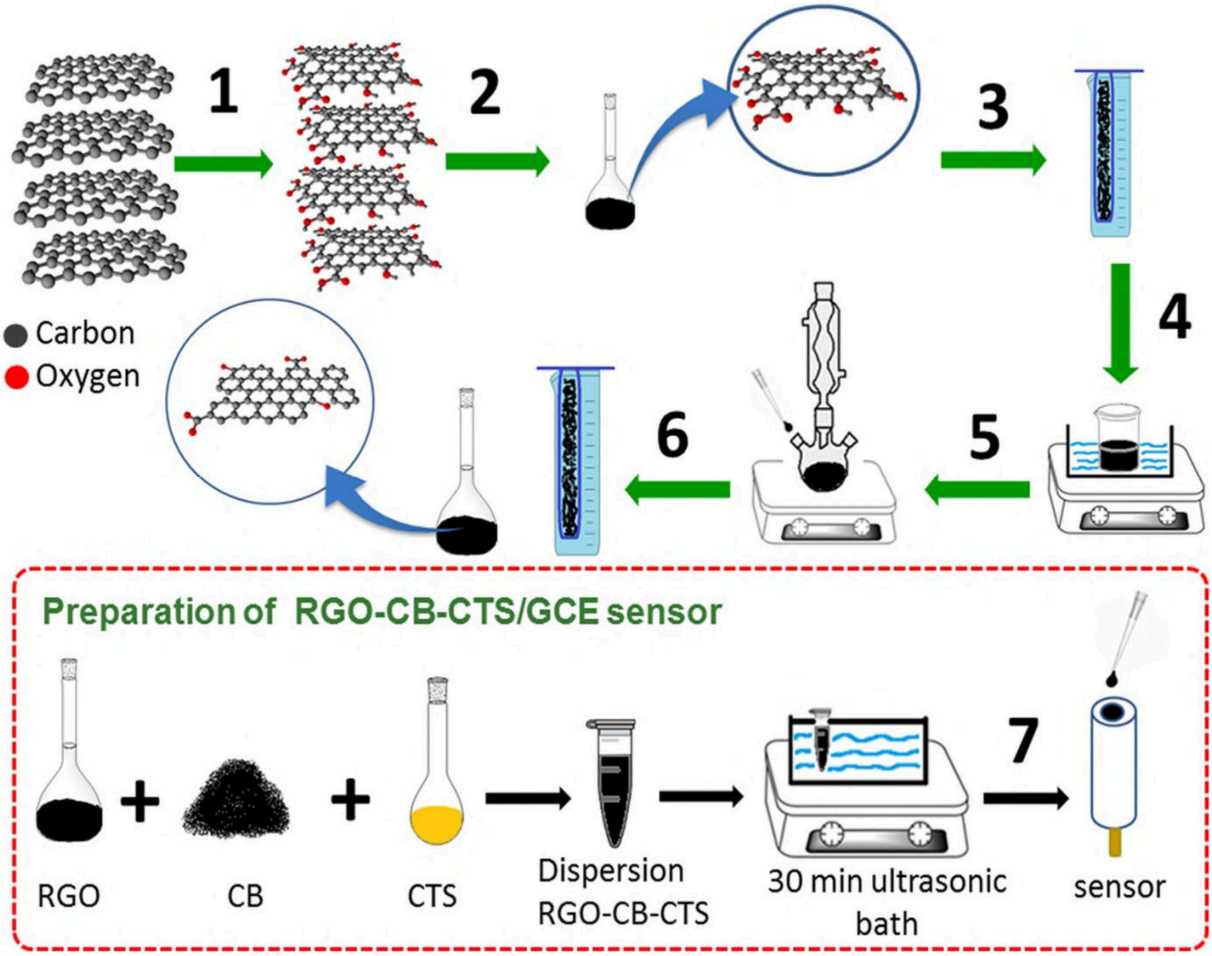


Figure 29. Schematic representation of the preparation of reduced graphene oxide and the RGO/carbon black/CTS composite modified GCE sensor fabrication process. Reproduced with permission from ref [251]. Copyright 2017 Elsevier.

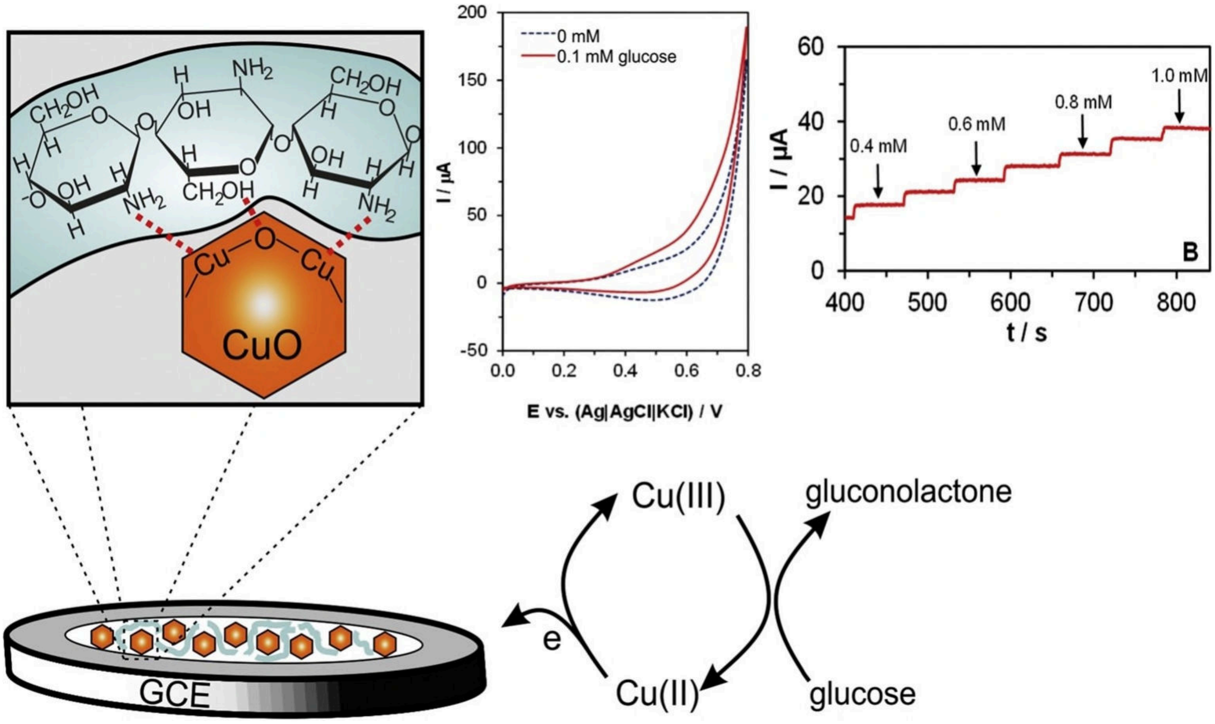


Figure 30. The fabricated novel a non-enzymatic glucose biosensor with the help of copper oxide-CH nanocomposites by a biomimetic approach. Reproduced with permission from ref [252]. Copyright 2018 Elsevier.

4.1.2. Biosensor Applications of Cellulose-Based Nanocomposites

Cellulose is one of the non-toxic organic bio-renewable material. It is the most abundant colourless resource on earth. [253] Furthermore, because it has some important features such as mechanic stability, flexibility, biocompatibility, biodegradability, it is often used in industrial applications such as pharmaceutical, biomedical, biotechnology, textile and food technology. Cellulose can be easily obtained particularly by two different sources as vegetable and bacterial and can be used in nanocomposite structure as crystalline cellulose, fibre, nanofibrils, cellulose fibres, and modified cellulose structures. Recently, the cellulose sensor has been discovered because of the suitability for flexible electronic applications as a smart material. Cellulose is usually in the structure of a hybrid nanocomposite along with the materials increasing the electron transfer such as inorganic oxides, carbon nanotubes and graphene for sensor applications. Researches on this subject have increased with the incremental demand for environmentally friendly and flexible materials in modern electronic applications.

Kafy et al. [254] preferred to use the structure of cellulose/graphene nanocomposites for sensor applications. Since the graphene sheets have important electrical properties such as electron transport, high catalytic and electrocatalytic activity, they are used in the applications of electrochemical supercapacitor, microelectronic and optoelectronic devices as gas sensors, chemosensor, and biosensors. Currently, polymer-graphene composite materials are being researched and improved as a sensor in chemical and biomedical applications due to their low cost and flexibility. In this study, cellulose/graphene nanocomposites had been used due to their high mechanical, dielectric and electrical performances. The synthesized nanocomposites had been characterized by FTIR, XRD, and SEM. At the same time, synthesized nanocomposites had been evaluated as the solvent sensor by determining the varying capacitance measurements with the reaction between a variety of solvents (n-hexane, chloroform, toluene, acetone, and ethanol) and nanocomposites. At the end of the experiment, the highest capacitance variation had been observed in ethanol (polar) solvent, while the lowest capacitance variation had been seen in the n-hexane (nonpolar) solvent. From the study of Kafy et al., it is seen that since the production of synthesized nanocomposite material is quick, easy and sensitive, it can be used instead of expensive and disposable solvent sensors.

Having easy deformable structure, high adsorption on the electrode surface, being porous and biocompatible, cellulose had brought the consideration, not for only liquid analytes but also determining the availability of the components in the gas phase. In this area, ammonia, volatile organic molecules, toxic gases or even natural gas sensors had been studied. Ammonia is a colourless mater with a distinctive odour. Because of the strong smell of ammonia vapor, it is detected easily in high doses by people. However, the use of highly sensitive and selective sensors is required for the sensing of small amounts of ammonia. [255] In general, the detection of gaseous ammonia is carried out by infrared devices or potentiometric electrodes. However, these devices are expensive and slow. [256]

Mun et al. [257] synthesized cellulose-titanium dioxide (TiO_2)-MWCNT for the detection of ammonia gas. The nanocrystalline structure of TiO_2-MWCNT nanocomposites was determined with XRD and TEM. Then, cellulose was doped into this nanocomposite structure. Cellulose-TiO_2-MWCNT hybrid nanocomposites had been prepared and used as an NH_3 gas sensor at room temperature. Ammonia gas which is in the range between 50 ppm and 500 ppm had been quickly and effectively determined with the prepared sensor. The study team demonstrated that these hybrid nanocomposites which are flexible, inexpensive, highly selective and reproducible could be applied as a gas sensor.

Bacterial-cellulose nanofibre-SnO_2 composites were successfully prepared by Sakwises et al. For Ni^{2+} adsorption and electrochemical detection, these composites were used as a novel platform (Figure 31). [258] To determine their physicochemical properties, the composites were characterized via various techniques such as XRD, TGA, atomic force microscopy (AFM), SEM and energy dispersive X-Ray spectroscopic (EDX) analysis. The obtained results indicated that SnO_2 particles (1wt%-10wt%) were successfully embedded onto the bacterial-cellulose surface. Also, the morphological analysis showed the presence of the SnO_2 particles within the prepared composites and these composites exhibited a uniform topography, porosity and surface roughness. For determination of the Ni^{2+} adsorption, CV measurements were carried and the relationships between the current-response signal and applied potential were investigated. The authors proposed that these prepared composites can be utilized as an appropriate carrier for Ni^{2+} adsorption and the direct electrochemical Ni^{2+}detection system. [227]

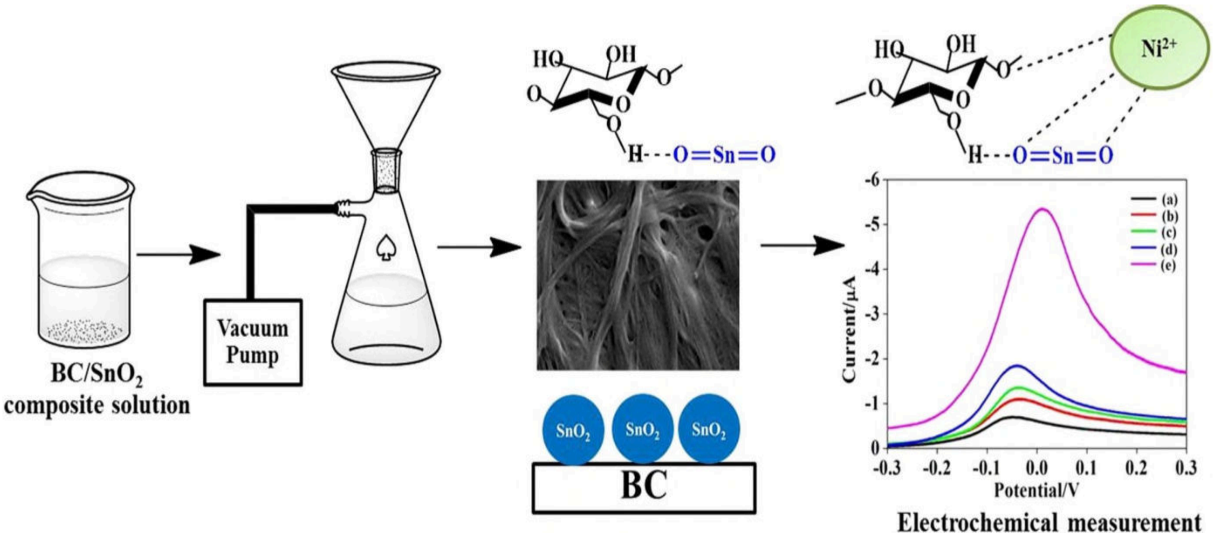


Figure 31. The bacterial-cellulose nano**fibre**-SnO2 composites for Ni^{2+} adsorption and electrochemical Ni^{2+} determination. Reproduced with permission from ref [258]. Copyright 2017 Elsevier.

In another study, the graphene oxide/carboxymethyl cellulose/glutathione (rGO/CMC/GSH) modified electrode was fabricated for the detection of Cd (II) (Figure 32). [259] The prepared electrode showed high reproducibility, selectivity and stability for the detection of Cd (II) due to the prepared nanocomposite's good stabilizing ability, chelating property and high surface area. The detection limit for the prepared rGO/CMC/GSH electrode was 0.05 nM and its sensitivity was 4.5 μA/nM. The developed rGO/CMC/GSH electrode-based sensor was also applied to detect Cd^{2+} in the milk samples, and egg albumin and the obtained Cd^{2+} measurement results showed good agreement with the measurement results of AAS method.

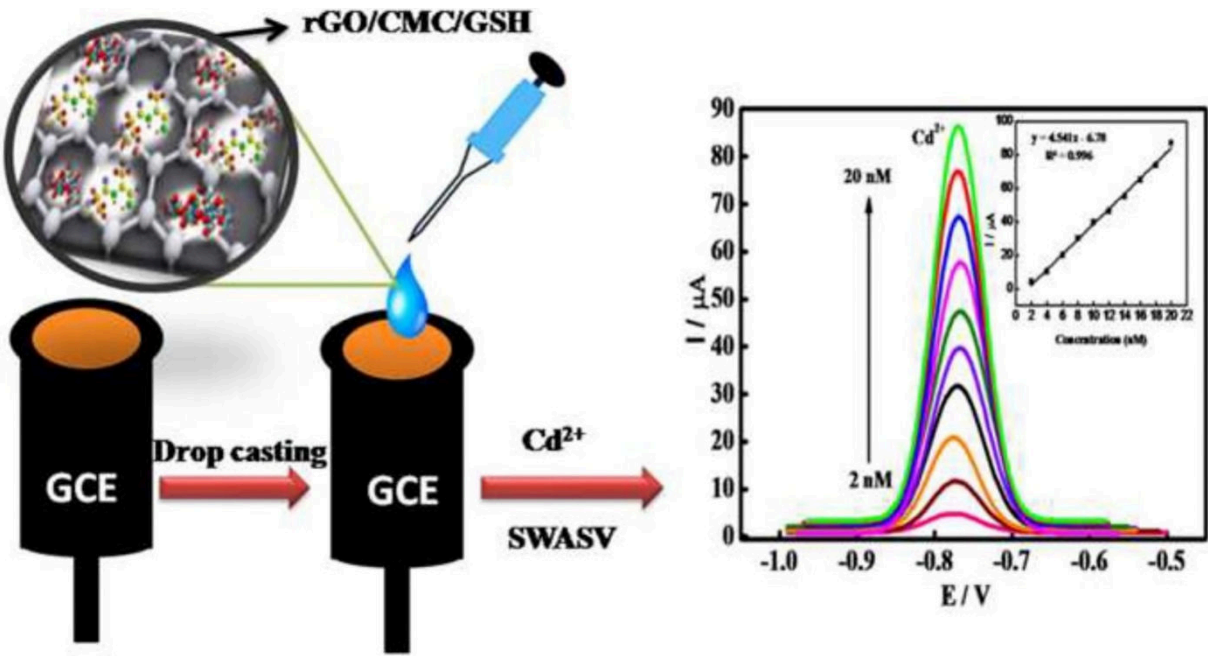


Figure 32. The preparation of the reduced graphene oxide/carboxymethyl cellulose/glutathione modified electrode and the results of Cd (II) peak with increase Cd(II) concentration by this electrode. Reproduced with permission from ref [259]. Copyright 2018 Elsevier.

Colloidal semiconductor quantum dots (QDs) are very important materials for electronic and optoelectronic application and they are known to be widely used in both optical and electrochemical biosensors. QD exhibit distinctive properties such as light conductivity, high surface area, good surface modification properties, and optical propagation due to the interesting excitation wavelength. Recently, an innovative electrochemical sensor based on nanocrystalline cellulose decorated QDs for phenol determination was reported (Figure 33). The biosensor was fabricated by immobilizing tyrosinase enzyme onto QDs nanocomposite. The fabricated sensor exhibited high electrocatalytic activity towards phenol, which is accredited to good conductivity, high surface area and biocompatibility of the nanocomposite. The QDs based sensor displayed good detection response with a detection limit of 0.082 μM, 0.078 μA/μM sensitivity and a linear detection range up to 5-40 μM. [260]

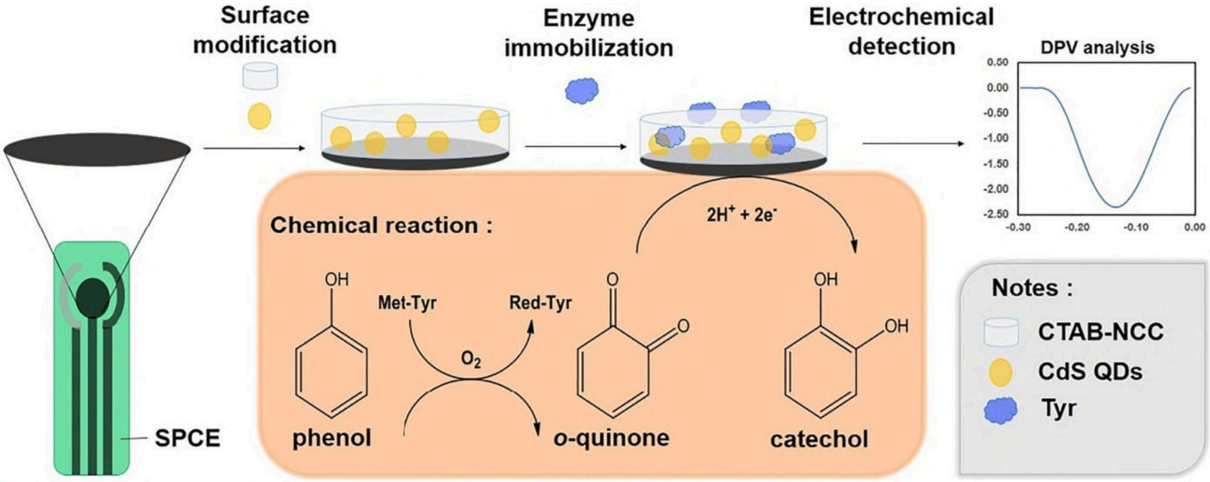


Figure 33. Schema of preparation and measurement mechanism of the nanocrystalline cellulose decorated QDs biosensor. Reproduced with permission from ref [260]. Copyright 2019 Elsevier.

4.1.3. Biosensor Applications of β-Cyclodextrin-Based Nanocomposites

Electrochemical sensors are simple and effective instruments for the rapid determination of various chemicals. New nano-materials in the nanosensor applications have been improved together with the development of nanotechnology science. While the materials to be used as sensors are synthesized, there is generally an orientation on the use of natural, cheap and bio-renewable resources. One of these resources is also β-Cyclodextrin. Cyclodextrin, which consists of seven glucose units and is produced by the enzymatic degradation of S, is a bio-renewable cyclic oligosaccharide having the hydrophilic outer part and hydrophobic inner part. [261,262] Cyclodextrin are extensively used in several industrial applications such as hydrogels, hydrophobic drug carriers, drug targeting, separation and detection, pharmaceutical reinforcements, paint purification, and electrochemical sensors.

Wang et al. [263] synthesized β-Cyclodextrin/Fe_3O_4 hybrid magnetic nanocomposites as a tryptophan sensor (Figure 34). Tryptophan is a non-essential amino acid constituting proteins and is an essential component that is indispensable to ensure the nitrogen balance in human nutrition. However, when taken in high doses of tryptophan, it may cause some side effects such as loss of appetite, nausea, drowsiness and dizziness. [264] Hence, sensitive simple and rapid detection of tryptophan is very important in terms of public health. To determine tryptophan, some analytical methods such as liquid chromatography, fluorescence spectroscopy, capillary electrophoresis measurements and electrochemical analysis are used. Among these methods, electrochemical methods are the most preferred techniques due to the high sensitivity, simple and easy implementation in recent years. Therefore, new materials are needed for electrochemically identifying of tryptophan. In electrochemical sensor applications, polymers, nanocomposites, and inorganic polymeric films are used for the modification of the electrode. Nanocomposites are very promising and important materials for the design of electrochemical sensors because of having a high surface area, better distribution, and functionalization properties. Therefore, Wang et al. prepared nanoparticle-based nanocomposite material for sensor applications. In nanocomposite material, they had used β-CDs a bio-renewable resource for its characteristics and Fe_3O_4 nanoparticles (MNPs), which showed the magnetic property, as reinforcement. In recent years, MNPs are among very interesting nanomaterials in terms of easy preparation, high adsorption ability, and electrical properties as electrochemical sensors and biosensors. The working team characterized the synthesized β-CD-MNPs hybrid nanocomposites with TEM, FT-IR, and TGA methods. β-CD grafted onto Fe_3O_4 magnetic nanoparticles had been used to determine tryptophan with modifying glassy carbon electrode by the electrochemical impedance spectroscopy method and cyclic voltammetry. β-CD-MNPs hybrid nanocomposites had increased the electron transfer amongst the solution and the electrode. Some important parameters such as the amount of nanocomposite, pH of the solution, and the rate of voltammetry scan had been also optimized. Under optimum conditions, tryptophan measurement concentration range, the detection limit and the consecutive 8 measurements of relative standard deviation for 1.0× 10^{-4} M tryptophan had been measured as from 8.0×10^{-7} to 3.0×10^{-4} M, 5.0×10^{-7} M and 4.2%, respectively. The procedure recommended by the study team had been successfully used for the detection of tryptophan and positive results had been obtained.

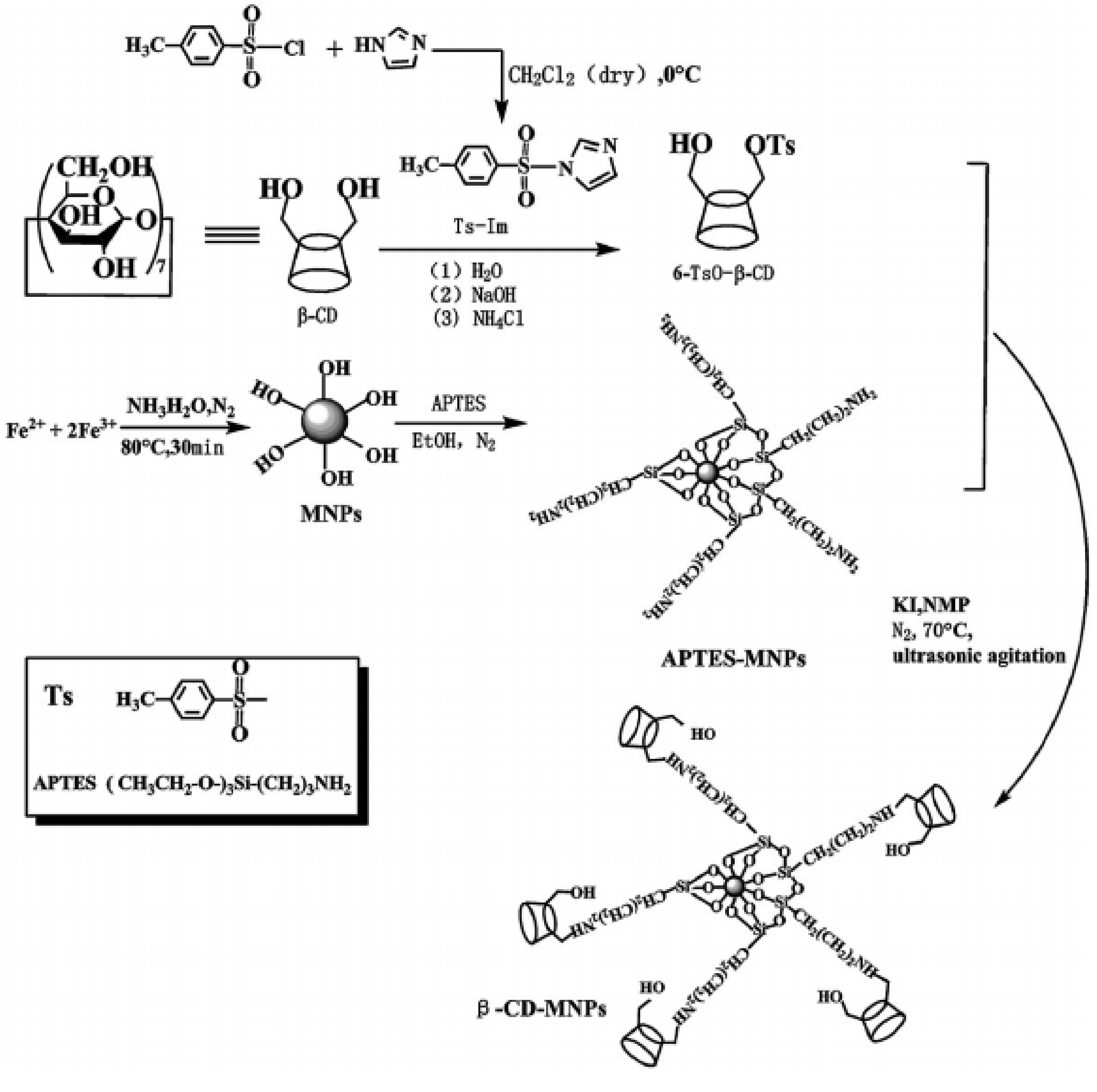


Figure 34. Preparation of β-CD-MNPs hybrid nanocomposites. Reproduced with permission from ref [263]. Copyright 2012 Elsevier.

Catechol (CT) is a natural phenolic compound that is found in tea, vegetables, fruits, tobacco, and some traditional Chinese drugs. [265] CT has a biological significance as it has the activity of some enzymes, antioxidants, and anti-virus features. However, when taken in high doses of CT, it causes toxic effects in both humans and other creatures. [264] Therefore, researches on the determination of CT have increased to protect living organism health, check food quality, and control of environmental pollution. Today, spectroscopy, liquid and gas chromatography are used for the determination of the CT level, but these methods are expensive and time-consuming. Instead of these methods, researches related to the production of fast, simple, cheap and sensitive sensor technology have increased. Han et al. [262] developed a nanocomposite modified sensor to determine CT, which is an important phenolic compound, with an electrochemical method. Nanocomposite structure was comprised of the bio-renewable natural oligosaccharide β-CD and cobalt ferrite ($Co_xFe_{3-x}O_4$) magnetic nanoparticles. Because of the cheap and good electro-active properties of cobalt (Co)-based nanomaterials and biocompatibility and selectivity properties of magnetic nanoparticles, they had been preferred in the structure of nanocomposite. Catechol measurement concentration range and detection limit had been measured as from 1-200 µM, and 0.12 µM. As a result, to determine catechol in water samples a nanocomposite modified sensor having the properties of high selectivity and repeatability had been designed.

Another study using bio-renewable β-CD in the nanocomposite structure had been performed by Zhang et al. [261] New β-CD/graphene nanocomposite films had been prepared to detect quercetin. Graphene had been used in the nanocomposite structure because of the high surface area and the electronic properties. Quercetin, a natural pentahydroxyflavone, is an important component found in various drinks, medicinal plants, flowers, fruits, and leaves. [266] Since quercetin shows some biological activities such as antioxidant, antitumor activity, estrogen, antiallergic and anti-inflammatory effect, it is a crucial component. However, its overuse had been reported to cause kidney cancer. [267] Therefore, the determination of the amount of quercetin is important in medical and food researches. For the scope of work, the morphology, physical properties and chemical structure of synthesized β-CD/graphene nanocomposite films had been characterized with instrumental analysis methods, and the electrochemical properties had been determined with differential pulse voltammetry and cyclic voltammetry measurement techniques. Under optimum conditions, the determination range for quercetin and the value of the detection limit had been measured as from 0.005 to 20 mM and 0.001 mM, respectively. The sensor had also exhibited good stability and high selectivity. As a result of the study, Zhang et al. reported that the sensor that was designed by them gave satisfactory results and could be used for the analysis of real samples in further studies.

Zhou et al. reported the 1-pyrenebutyrate based rGO/mercapto-β-CD/Au composite based electrode for the quantitative analysis of quercetin (Figure 35). The developed sensor showed that the linear response range for quercetin was from 0.005 to 0.4 μM. At the same time, the prepared sensor exhibited a low detection limit (1.83 nM). Furthermore, prepared nanocomposite based sensor also displayed very high sensitivity and good stability for the determination of quercetin and several other flavonoids do not interfere. [268]

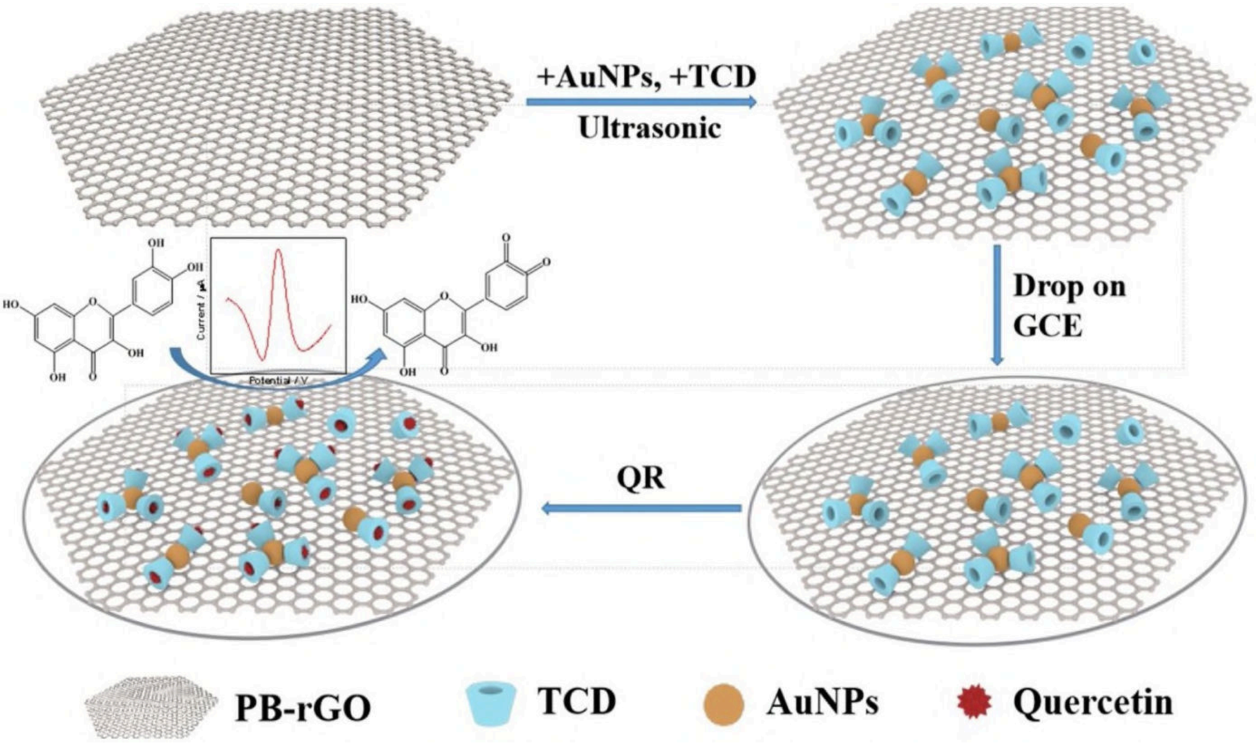


Figure 35. The preparation and sensing schema of the PB-rGO/TCD/AuNPs/GCE. Reproduced with permission from ref [268]. Copyright 2019 Elsevier.

In a recent study, Zhao et al. [269] using MoS_2-carbon nanotube@graphene oxide nanoribbons/HS-Cyclodextrin/graphene quantum dots composite film designed and developed a novel electrochemical sensor to determine ultrasensitive quercetin. Under optimal conditions, the linear response range for quercetin was from 2.0×10^{-9} to 1.6×10^{-6} M with a low detection limit of 8.2×10^{-10} M. In the practical application of this sensor, a satisfactory result was achieved for the determination of quercetin in the real samples such as juice and honey. Besides, the sensor displayed good repeatability, high selectivity, and good storage stability. Overall, the designed sensor is promising for the detection of quercetin in comparison with other counterparts.

Hui et al. [270] synthesized silver-β-Cyclodextrin/graphene (AgNPs-β-CD/GR) nanocomposite-based biosensors in their research. The prepared sensors had been used in the simultaneous determination of adenine and guanine bases. In the previous studies, it had been mentioned that β-CD and GR had been frequently used in electrochemical sensor design and nanocomposite structures because of their properties. In this study, especially for the detention of Ag nanoparticles, β-CD had been used and it prevented the leakage of these nanoparticles from the electrode surface during the application. Graphene created a conductive channel at the coating of the electrode surface and generating an electrocatalytic effect had allowed simultaneous analysis of adrenaline and graphene. At the same time, graphene had increased the electrode surface area by creating a highly porous surface. In this way, it enabled the determination of lower analytes concentrations.

DNA and RNA are well known for having vital functions such as transfer of the genetic features and *in vivo* protein synthesis. Adenine and guanine are the essential components of some DNA and RNA. [270] Therefore, the analytical determination of these two bases is significantly important in molecular biology, genetics, bioscience, and clinical analysis. The electrode which would be used as the sensor had been modified with the synthesized nanocomposite material and the measurements of both bases had been made by the differential pulse voltammetry method. The range for the determination and the detection limit of Adenine had been measured as 0.3-200 µM and 0.09 µM; whereas, the range for the determination and the detection limit of Guanine had been determined as 0.5-25 µM and 0.15 µM, respectively. These results had shown that that prepared nanocomposite materials have the potential to be used in the implementation of electroanalytical biosensors.

Polypyrrole (PPy) decorated graphene/β-CD composite film was fabricated with chemical oxidation method of PPy monomer (Figure 36) and its application in electrochemical detection of low concentration of mercury (II) was investigated by Palanisamy et al. [271] The developed sensor showed low LOD, high sensitivity, and broader linear response range to detect Hg (II). Even in the active metal ions presence, the sensor showed also good selectivity for the determination of Hg (II) amount. Additionally, the team reported that the LOD value of the prepared sensor was lower than the advised level of Hg (II) set by the U.S. EPA (Environmental Protection Agency) and the WHO.

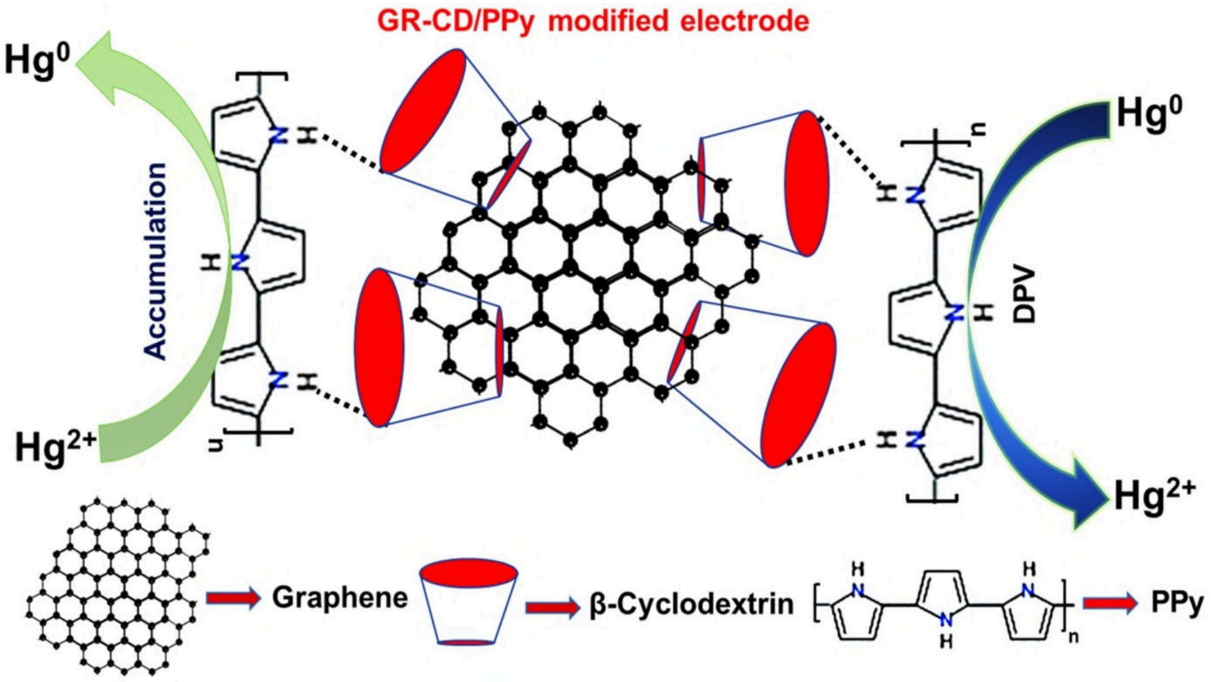


Figure 36. The possible Hg(II) detection mechanism of the GR-CD/PPy composite electrode. Reproduced with permission from ref [271]. Copyright 2017 Elsevier.

In recent years, copper oxide nanoparticles doped graphene(GR)-β-CD composites have been reported for the detection of metronidazole as an antibiotic drug (Figure 37). [272] The fabricated electrode displayed a linear electrochemical response between 0.002 and 210.0 µM concentration range and 0.6 nM metronidazole detection limit. The electrochemical results suggest that the prepared graphene(GR)-β-CD composites based electrode exhibited excellent catalytic activity, high selectivity and low reduction potential for the detection of metronidazole. Furthermore, the sensor was also effectively applied to determine the metronidazole amount in pharmaceutical tablets.

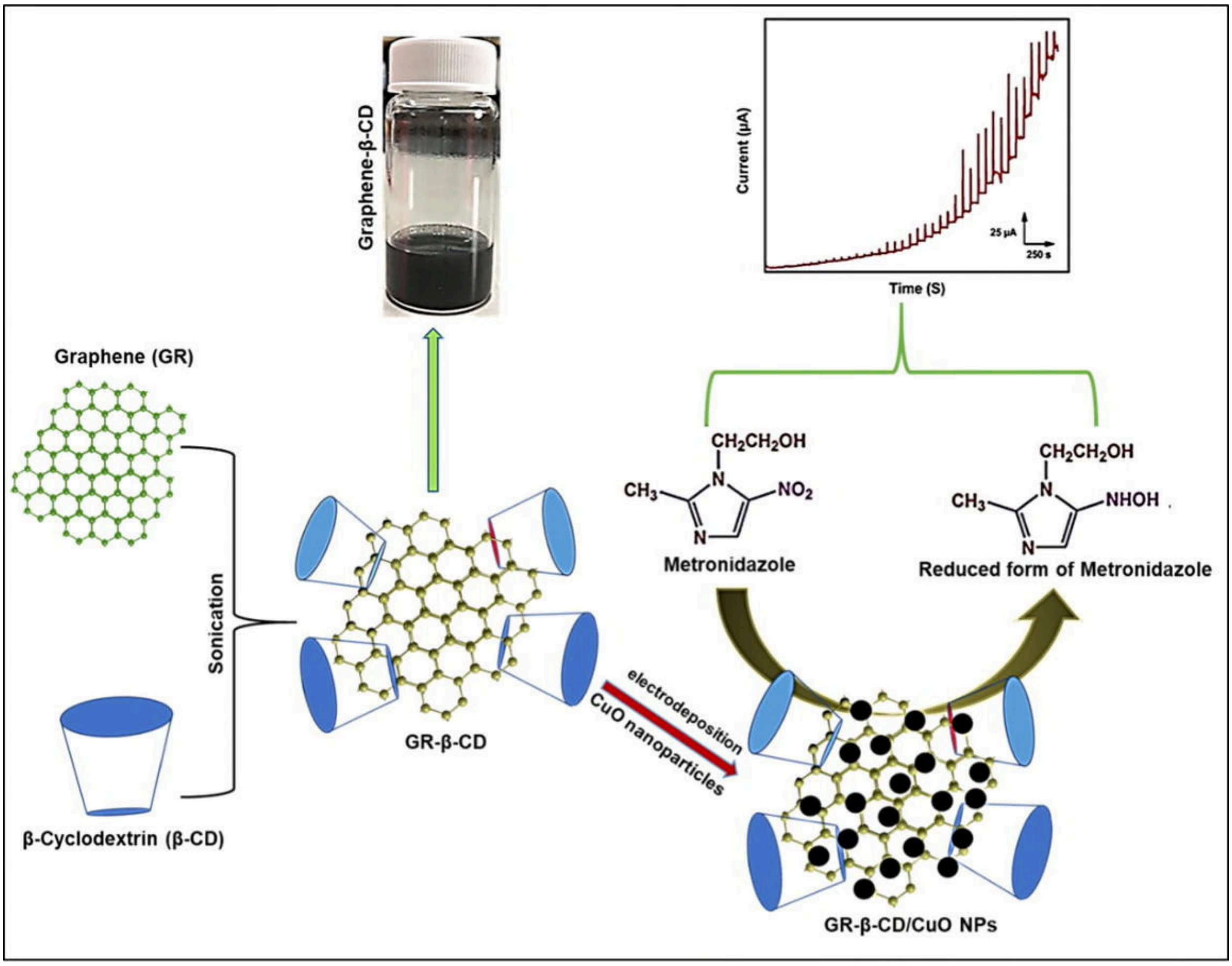


Figure 37. The CuO nanoparticles doped GR-β-CD composites for the detection of metronidazole. Reproduced with permission from ref [272]. Copyright 2018 Elsevier.

Karthika et al. [273] synthesized CuO/β-CD nanocomposites via the sonochemical method to develop an electrochemical sensor for L-tyrosine detection. The nanocomposites were characterized using FE-SEM, UV–vis, FT-IR, Raman, XRD and mapping analysis methods. In comparison to the CuO, modified β-CD, and bare GCE electrodes, the CuO/β-CD modified electrode showed higher electrocatalytic activity towards the L-tyrosine. According to obtained measurements, the CuO/β-CD modified electrode exhibited an outstanding amperometric i-t current response to determine the L-tyrosine with a broad range from 0.01 to 100 μM, high sensitivity 442 μA $\mu M^{-1} cm^2$ and little detection limit (0.0082 μM). The electrode exhibited decent repeatability, selectivity, stability, and reproducibility. Besides, it displayed good sensibleness to detect L-tyrosine in the food samples, urine samples and blood serum.

4.1.4. Biosensor Applications of Guar Gum-Based Nanocomposites

Biopolymers are the most frequently used structures for designing multifunctional materials because they are biocompatible, biodegradable, hydrophilic, inexpensive and have chelating abilities to name a few. Guar gum (GG) is a biopolymer structure containing galactose and mannose units. GG is a commonly used source to prepare the advanced materials due to the strong hydrogen bonds, good film properties, emulsifying and stabilizing agents. Besides, GG has a wide range of pH which may be compatible with various inorganic and organic materials, and exhibit high solubility and viscosity properties. Due to all these features and being a bio-renewable resource, GG is an important polymer for nanocomposite materials and their advanced applications. Especially, they are often used in the preparation of the sensor structures, the distribution of the active sensitivity molecules, the attachment onto the electrode surface and the forming of stable films on the surface.

Malik et al. [274] synthesized SnO_2/Guar gum hybrid nanocomposite materials using SnO_2 nanoparticles. They had prepared appropriate sensors for the determination of hydrazine using this synthesized material to modify the electrode surface. Hydrazine and its derivatives, pharmaceutical by-products, antioxidants, pesticides, plant growth regulators, reducing agents and corrosion inhibitors are of great importance. However, sometimes hydrazine can be toxic and carcinogenic. Thus, the hydrazine affects the brain, DNA, blood, nerve system and cause some disorders. [275] In the diagnosis and treatment of all of these diseases, prepared sensor structures are very important. In the study, the prepared SnO_2/Guar gum hybrid nanocomposite based sensor showed low detection (in the range of 2–22 mM), suitable low detection limit

(2.76 mM) and high sensitivity (5.72 μA cm^{-2}) for hydrazine determination. In other guar gum-based sensor structures, nanoparticles such as SiO_2, TiO_2 and CeO had been doped into guar matrix components and relatively high efficiency of the sensor was obtained.

Samples of biosensor applications of nanocomposites from bio-renewable resources are also given in Table 6 as summary information.

Table 6. Biosensor applications of nanocomposites from bio-renewable resources

Composite	**Analytes**	**Electrode**	**Method**	**Linear range**	**LOD**	**Sensitivity**	**Ref.**
NanoCeO$_2$-CH	Cholesterol	ITO	CV, EIS	10–400 mg/dL	5 mg/dL	47 μA/mg dL^{-1}cm^{-2}	225
CH–Fe$_3$O$_4$	BPA	GCE	CV, DPV	0.05–30 μmol dm^{-3}	0.008 μmol dm^{-3}	-	233
GNPs-MWCNT-CH	BPA	GCE	CV, DPV	0.1-100 μM	0.05 nM	-	235
CH-Ag	Hg (II)	-	Colorimetric	-	7.2×10^{-8} M	-	236
MnOx/MWCNTs/CH	Cr (III)	GCE	CV, hydrodynamic amperometery	3 μM-200 μM	0.3 μM	18.7 nA μM^{-1}	245
Quantum dots/CH	Catechol	GCE	EIS	1.0×10^{-9}-2.0×10^{-5} M	0.3 nM	561±9.7 mA M^{-1}	248
Au-CH	Caffeic acid	Gold	CV, DPV	5.0×10^{-8}-2.0×10^{-3} M	2.50×10^{-8} M	-	249
MWCNT–SnO$_2$–CH	DNA	Gold	CV, EIS	1.0×10^{-11}-1.0×10^{-6} M	2.5×10^{-12} M		250
RGO-CB-CH	DA	GCE	CV, SWV	3.2×10^{-6}-3.2×10^{-5} M	2.0×10^{-7} M	-	251

	PAR			2.8×10^{-6}-1.9×10^{-5} M	5.3×10^{-8} M		
CuO-CH	Glucose	GCE	CV, AD	0.050-1 mM	11 μM	503 μA.mM/cm^2	252
rGO/CMC/GSH	Cd (II)	GCE	CV, EIS	2–20 nM	0.05 nM	4.5 μA/nM	259
NCC/CdS QDs	Phenol	SPCE	CV, EIS, DPV	5-40 μM	0.082 μM	0.078 μA/μM	260
β-CD/Fe_3O_4	Tryptophan	GCE	CV, EIS	8.0×10^{-7}-3.0×10^{-4} M	5.0×10^{-7} M	-	263
β-CD-cobalt ferrite	Catechol	GCE	CV, DPV	1-200 μM	0.12 μM	-	262
β-CD/graphene	Quercetin	GCE	CV, DPV	0.005-20 mM	0.001 mM	-	261
rGO/mercapto-β-CD/Au	Quercetin	GCE	CV, DPV, EIS	0.005-0.4 μM	1.83 nM	-	268
MoS_2-CNT@GO/HS-CD/graphene QDs	Quercetin	GCE	CV, DPV, EIS	2.0×10^{-9}-1.6×10^{-6} M	8.2×10^{-10} M	-	269
AgNPs-β-CD/GR	Guanine Adenine	GCE	CV, DPV	0.3-200 μM 0.5-250 μM	0.09 μM 0.15 μM	-	270

GR-β-CD/CuO NPs	Metronidazole	GCE	CV, Amperometry	0.002-210.0 μM	0.6 nM	-	[271]
CuO/β-CD	L-tyrosine	GCE	CV, Amperometric	0.01-100 μM	0.0082 μM	442 μA μM^{-1}cm^{2}	[272]
SnO$_2$/Guar gum	Hydrazine	ITO	CV, DPV	2–22 mM	2.76 mM	5.72 μA cm^{-2}	[274]

4.1.5. Other Sensor Applications

Researchers have recently focused on the development of flexible humidity, temperature, and mechanical (strain, compress, etc.) sensors as well as biosensors. Dai et al. [276] developed CH/zinc oxide/single-walled carbon nanotube composite film based chemiresistive humidity sensor. They characterized the developed sensor by using XRD, SEM and FTIR techniques. Additionally, they performed humidity sensing properties of the sensor in a broad range of relative humidity (RH) (11%, 23%, 33%, 43%, 52%, 67%, 75%, 86%, and 97%) at room temperature. According to the results obtained, it displayed high sensitivity and good reproducibility. Hence, the authors suggested that the sensor may be further improved by a distinct dispersion technique or composite structure optimization, such as hierarchical structure or organic-inorganic coaxial hybrid because of good sensing performance.

Qi et al. have fabricated a quartz crystal microbalance (QCM) humidity sensor using the graphene quantum dots and CH composites [277]. The composite was examined for structural and morphological characteristics by using FTIR, SEM, TEM, and HR-TEM. The humidity sensor displayed short response/recovery time (36 s/3 s), high response sensitivity (a frequency shift of −3291 Hz at 95% RH), tiny humidity hysteresis (~1.6% RH), long-term stability, excellent reproducibility, and reversibility. As a result, it was concluded that the fabricated QCM sensor is quite reliable to monitor water vapor content in a broad humidity range.

Sadasivuni et al. [278] proposed cellulose/rGO composite films and investigated their morphology and structural properties through FTIR, XRD, SEM and Raman spectra methods for flexible temperature sensor application. The temperature sensor exhibited linearity concerning the temperature change between 25 and 80 °C. In conclusion, the authors anticipated that such devices exhibit high potential to be used in a number of applications including wearable devices and electronic equipment.

Besides the above studies, some sensors were reported to simultaneously measure relative temperature and humidity. For instance, Mahadeva et al. [279] fabricated flexible temperature and humidity sensor using cellulose–polypyrrole nanocomposite. With the increment in the humidity, the capacitance of the flexible sensor was found to be increased. Besides, similar results were obtained for change in temperature. Moreover, it displayed the best linearity and superior reversibility with good response and recovery behavior.

In another example, Li et al. [280] produced an optical fibre sensor based on CMC/CNT film to simultaneously measure the temperature and relative humidity. The humidity sensitivity of the proposed sensor with CMC film was found to be 170.55 pm/%RH. On the other hand, the CMC/CNTs composite film sensor exhibited the sensitivity of 230.95 pm/%RH with an enhancement of 35.41%. On the other hand, the sensor can also simultaneously measure the temperature having a sensitivity of 26.35 pm/°C.

As an example of mechanical sensors, Zheng et al. [281] used cellulose nanofibres and graphene co-incorporated poly (vinyl alcohol)-borax hydrogel to prepare self-healing and highly stretchable strain sensors. The strain sensor showed superb viscoelasticity (3.7 kPa storage modulus), great stretchability (break-up elongation up to 1000%), high healing efficiency (97.7 ± 1.2%), and fast self-healing ability (20 s). The hydrogel strain sensor can be used for several promising applications such as in intelligent wearable electronics.

In another study, Biswas et al. prepared a strain sensor using flexible ZnO nanowire-cellulose paper composite [282]. The developed strain sensor exhibited high gauge factor, good stability, and good repeatability. Therefore, the proposed robust and sensitive strain sensor can be utilized in the fields of MEMS devices, biomedical sciences, and structural health monitoring to name a few.

4.2. Chemistry, Structure and Energy Storage Applications

Energy is an imperative factor in the development of both developed and developing countries. With the increase in the human population and life quality, energy is needed in much more amount. At the same time, standard energy resources are based on fossil fuels and are also limited. Furthermore, these fuels cause pollution and global warming. Therefore, renewable energy storage, conversion materials, and their devices are very useful. To prevent this energy crisis, many scientific research centres worldwide are already funded on new solutions and also improved in the existing energy sector. These problems can be solved in two ways. Firstly, energy can be efficiently converted from endless sources such as oxygen reduction reaction, solar power, and water to the applied forms such as electricity and fuel. For this purpose, the fuel cells, solar cells, and water divider catalysts (water splitting catalysis) are the most widely used materials. [283–285] Secondly, economic, environmentally friendly, practice and high-performance energy storage devices are required. Most of these properties are in renewable energy resources. In particular, lithium-based batteries such as lithium-ion, lithium-air, and lithium-sulphur are the most useful and promising devices for storage purposes. [286–288] Another important and efficient energy storage devices are supercapacitor capable of storing and eliciting energy in a few seconds. [289]

4.2.1. Energy Storage Applications of Chitosan-Based Nanocomposites

Electrochemical capacitors having high power and energy density are regularly used as a versatile solution for emergency power applications. Due to the physicochemical properties of amino polysaccharide CH, one of the bio-renewable resources is an important polymer for the production of electrochemical capacitors. The crystallinity number and the degree of deacetylation of repeating glucosamine units of the CH are other important properties. Hassan and his team [290] synthesized the organic-inorganic nanocomposite consisting of the organic portion from CH and an inorganic portion from MnO_2 for electrochemical capacitors and energy storage applications. For electrochemical processes, manganese oxide compounds have attracted considerable interest as active electrode materials owing to their capacitance, low cost, abundance and environmentally friendly. MnO_2-CH (low and high molecular weight of the films) hybrid nanocomposite films had been synthesized by Hassan and his team with a one-step cathodic electrodeposition method on nickel foam substrate for the applications of electrochemical capacitors. It had been reported that MnO_2-CH hybrid nanocomposite films showed better specific capacitance and speed capability compared to MnO_2 films without CH and the highest capacitance value was determined as 424 F/g at 1 mA/cm^2. Nanocomposite film had shown a very stable capacitance feature by being charged and discharged over 400 cycles and only 3% of the capacity loss had been seen at 3 $mA.cm^{-2}$. Moreover, it had been found that CH enhanced the transition of electrons and ions and porous films with no crack were obtained. In another study, to obtain supercapacitor from bio-renewable sources, Pandiselvi et al. [291] researched the supercapacitor properties of CH-ZnO/polyaniline (CH-ZnO/PANI) triple nanocomposite materials. CH-ZnO/polyaniline composites had been prepared after being doped with ZnO and CH in different proportions using a sample preparation method by *in situ* polymerizations of aniline. Chemical structure, morphology and surface properties of prepared CH-ZnO/PANI nanocomposites had been thoroughly characterized using SEM, EDXS, Fourier transform infrared spectroscopy, N_2 adsorption/desorption measurement, UV-Vis spectroscopy, TEM, X-ray diffractometric, and thermal analysis. The electrochemical properties of the CH-ZnO/PANI nanocomposites had been investigated using electrochemical impedance spectroscopy and cyclic voltammetry. In addition, galvanostatic charge-discharge measurements were also performed. The maximum specific capacitance of $CH_{0.12}$-$ZnO_{2.5}$/PANI had been measured as 587.15 F g^{-1} cm in the potential range of 0-0.8 V, at the capacitance value of 175 mA cm^{-2} and the capacitance value of $CH_{0.12}$-$ZnO_{2.5}$/PANI electrode had been deteriorated about 80% after 1000 cycles. The specific capacitance and cyclic voltammetry performance of $CH_{0.12}$-$ZnO_{2.5}$/PANI structure increased since CS macromolecule had acted as a bridge between ZnO nanocomposites and PANI.

In another study, Hosseini and Shahryari prepared high-performance supercapacitor based on CH/GO-MWCNT/polyaniline ternary nanocomposite (Figure 38) [292]. The specific capacitance of the obtained nanocomposite was obtained as 609.2 F/g (48.5 m.F/cm^2) at a scan rate of 10 mV/s^1. Moreover, the prepared nanocomposite showed great stability with a reduction of only 4% after 500 times due to its porous structure and pseudocapacitive mechanism of charge-storage.

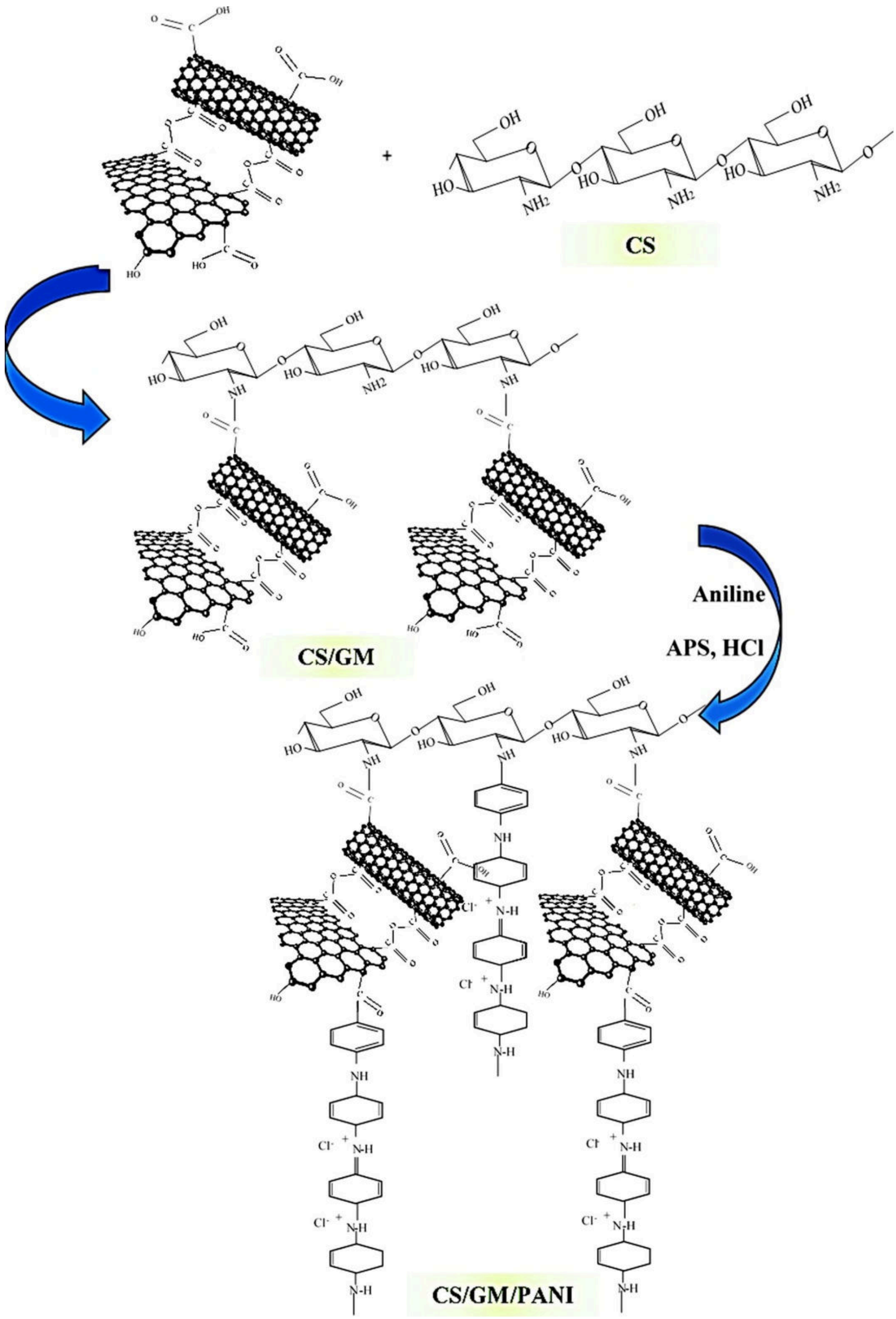


Figure 38. Preparation of the CS-based nanocomposites. Reproduced with permission from ref [292]. Copyright 2017 Elsevier.

In another study, Torvi et al. prepared a series of binary (CH/polyaniline) and ternary (CH/GR/polyaniline) nanocomposites by using *in-situ* polymerization of aniline (Figure 39). [293] They also characterized physicochemical properties of the nanocomposites with FTIR, XTD, TGA, and SEM. The electrical conductivity of CP_5 and CG_3P composite samples was recorded as 4.165×10^{-1} and 2.9745 S/cm, respectively. CG_3P composite exhibited more specific capacitance than PANI (495 F/g) and CP_5 (939 F/g). Moreover, it retained 88% of the initial capacitance after repeating 1000 cycles.

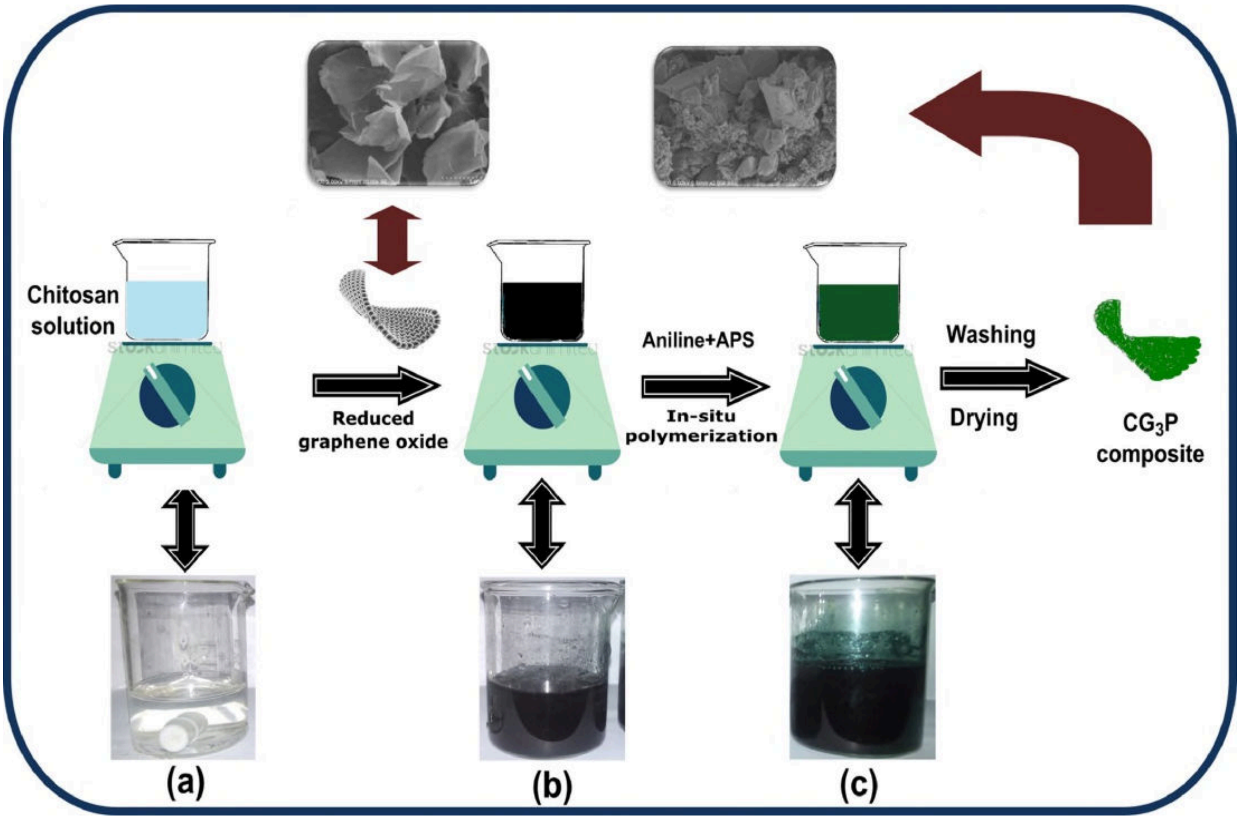


Figure 39. The synthesis steps of CGP nanocomposites by in-situ polymerization and their photographs. Reproduced with permission from ref [293]. Copyright 2018 Elsevier.

In recent work, Suneetha and Vedhi prepared Zn doped iron oxide/GO/CH nanocomposite by simple solution mixing-evaporation method for supercapacitor application. [294] They investigated the structural properties and electrochemical behaviours of the synthesized nanocomposites. The obtained results showed that the Zn doped iron oxide/GO/CH nanocomposite displayed good adherent, high thermal stability, and excellent synergistic super capacitive behaviours.

In another recent study, Yu et al. [295] prepared N-doped rGO/C@Silicon (Si) composite using bio-renewable CH for lithium-ion batteries to overcome the shortcomings of Si. Here, while CH was used as the donor of nitrogen and carbon, rGO/C was responsible for conductivity and supporting of the composite materials. N doping can efficiently increase the electrode interface and wettability of electrolyte. According to the obtained results, the proposed N-doped rGO/C@Si anode material exhibited higher cycling performance (1115.8 mAh g^{-1} after 150 cycles at 420 mA g^{-1}) and an improved rate capability (1077.4 mAh g^{-1} at 4200 mA g^{-1}).

4.2.2. Energy Storage Applications of Cellulose-Based Nanocomposites

Cellulose as a bio-renewable biopolymer is an inexhaustible resource of raw materials for numerous eco-friendly devices. [296] Cellulose-based composites have the potential to be widely used in coating, laminate, optical films, pharmaceutical, food packaging, and textile industries. [297–299] Cellulose is used in the design of flexible electronic materials due to its cheap, lightweight, relatively high thermostability, high absorption capacity, the variability of optical appearance and biocompatibility properties. [300] The chemical and morphological structure of these composite materials has the advantage of having very strong interaction with reinforcement particles, and therefore it is used much more compared to other bio-products. In the structure of bio-renewable-based nanocomposite materials, cellulose fibres, bacterial cellulose, nanocrystalline cellulose, and modified cellulose structures are used in electronic applications.

Xu et al. [301] synthesized BC-based nanocomposites by using BC produced by some bacteria using D-glucose as a good carbon source. BC has some features such as high purity, biocompatibility, crystallinity good mechanical property, and the ability to keep high water.

Besides, the chemical structure of BC provides an important and suitable hydrophilic matrix to form nanoparticles in the presence of hydroxyl and ether. Therefore, Xu et al. prepared polypyrrole-BC (PPy/BC) nanocomposites for making a flexible supercapacitor electrode. Conductive PPy/BC nanocomposites had been produced *in situ* with the oxidative polymerization of pyrrole.

The $FeCl_3$ and BC were used as oxidizing agent and matrix, respectively. The prepared materials were structurally and morphologically characterized by ATR-FTIR and SEM. Besides, the conductivity and electrochemical properties were studied. In a controlled reaction, the electrical conductivity of the prepared PPy/BC nanocomposite was measured as 3.9 Scm^{-1}. To explore the electrochemical property of PPy/BC structure, PPy/BC containing 106 wt.% of PPy had been used as a flexible electrode and cyclic voltammetry curves had been recorded at different scan rates. PPy/BC nanocomposites had shown a stable electrochemical behaviour across a wide range of potential ranging from -0.9 to 0.9 V. At the current density of 0.16 A g^{-1}, the maximum discharge capacity of PPy/BC membrane was measured as 101.9 mAh g^{-1}. Besides, significant degradation in the electrochemical performance of the obtained PPy/BC membrane electrode had not been seen as a result of measurements. Based on all these results, this nanocomposite membrane can be used as a flexible and wearable energy storage electrode.

Liew et al. [302] used cellulose nanocrystals (CNXLs), whose average size was about 6×6×150 nm, extracted from cotton as a bio-renewable resource in electrochemical applications. For this purpose, polyaniline-cellulose (PANI/CNXL) and poly (ethylene dioxythiophene)-cellulose (PEDOT/CNXL) nanocomposites had been synthesized. To determine the electrochemical properties, both synthesized nanocomposite structures had been characterized using different electrochemical techniques such as CV, electrochemical impedance spectroscopy, and galvanostatic charge/discharge measurement. PANI/CNXL and

PEDOT/CNXL nanocomposites showed higher capacitance and higher charge-discharge rates compared to cellulose-free electrodes.

Kafy et al. [303] used cellulose as a bio-renewable resource. They designed cellulose modified GO nanocomposites based on energy and memory storage material. Nanocomposites had been prepared with a simple casting/solvent evaporation procedure and were structurally characterized. The dielectric and ferroelectric properties of nanocomposites including bio-renewable resources had been controlled with the changes in temperature and voltage. These features can benefit from energy and memory storage areas. The study team had reported that the cellulose modified GO nanocomposites were quite suitable materials for environment-friendly energy storage devices.

Yu et al. prepared sodium carboxymethyl cellulose/collagen-based magnetic composite aerogel that was doped with N to develop an electrochemical supercapacitor (Figure 40). [304] The specific surface area, saturation magnetization and pore-volume for the selected sample were determined as 589.6 m^2/g, 11.38 emu/g, and 0.27 cm^3/g respectively. In a 6 M KOH electrolyte, the sample exhibited a specific capacitance of 185.3 F/g at the current density of 0.5 A/g. Furthermore, after 5000 charges/discharge cycles, it maintained 90.2% of the initial specific capacitance. All results indicate that the prepared sodium carboxymethyl cellulose/collagen composite based aerogel can be used as a supercapacitor for application due to the ease-to-prepare and low-cost.

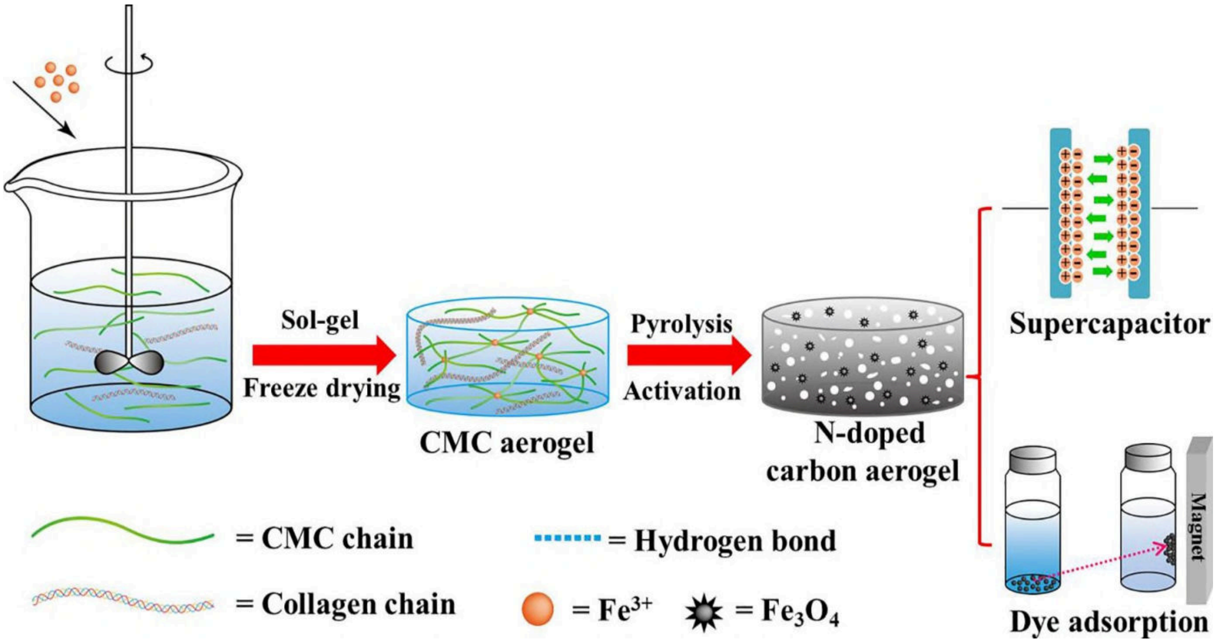


Figure 40. The preparation methods of magnetic N-doped carbon aerogel from sodium carboxymethyl cellulose/collagen composite aerogel. Reproduced with permission from ref [304]. Copyright 2018 Elsevier.

In another work, Li et al. synthesized core-shell nano fibrillated cellulose/ polypyrrole (PPy)/tubular graphitic carbon nitride composite film by using a simple polymerization method (Figure 41). [305] The electrochemical performances of the obtained electrode were investigated in detail and these electrodes showed high capacitance of 2.53 F/cm^2 at the current density of 5 mA/cm^2, equivalent to a specific capacitance of 158 F/g.

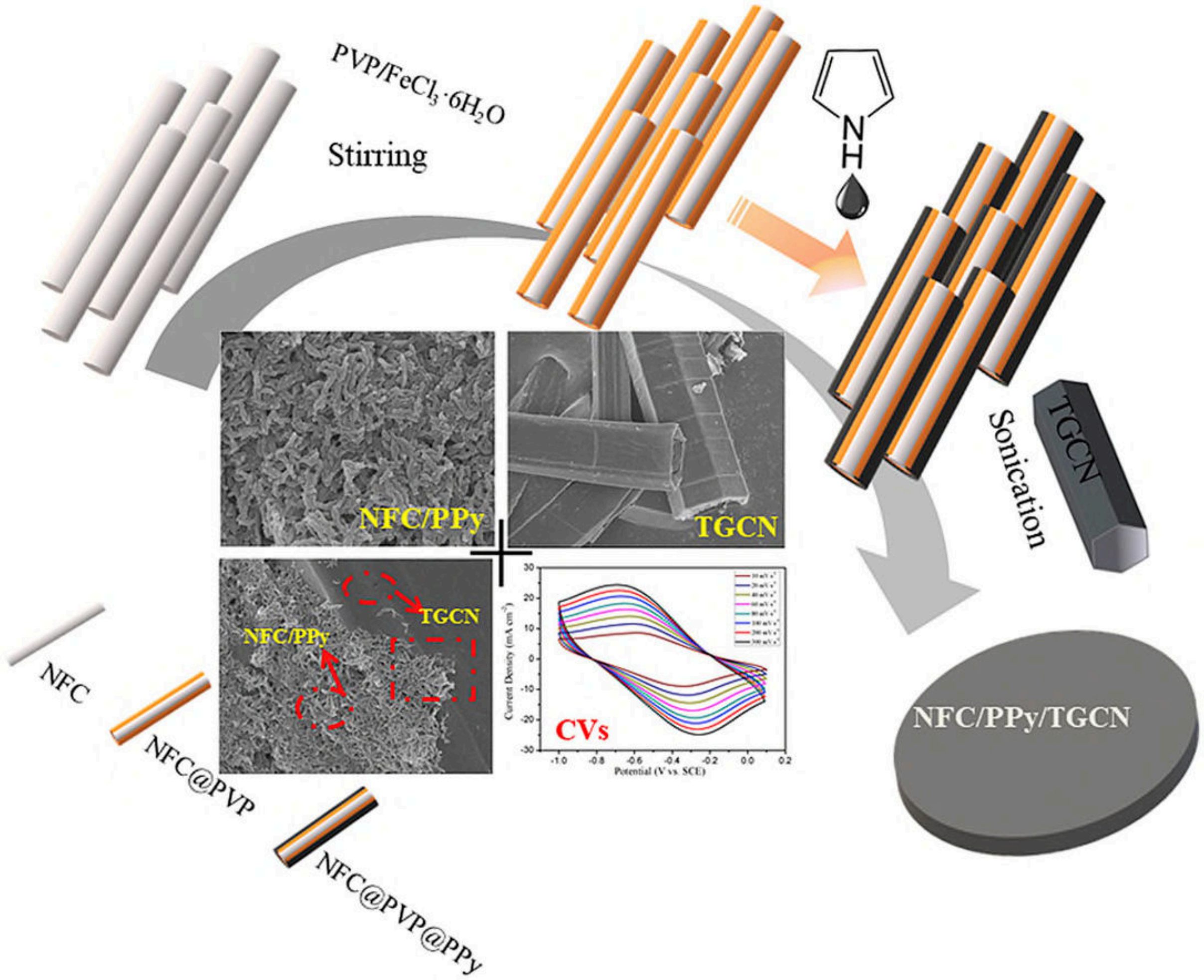


Figure 41. Schematic preparation steps of core-shell NFC/PPy/TGCN composite film and their SEM images. Reproduced with permission from ref [305]. Copyright 2019 Elsevier.

In a similar study, a fibre composite electrode of PPy@cobalt oxyhydroxide/cellulose was prepared by the liquid-phase reduction method and characterized by using FTIR, SEM and XPS techniques. Besides, this electrode was compared with previously reported conductive polymers electrodes. The composite electrode showed outstanding electrochemical properties with high specific capacitance as well as capacitance retention. A maximum specific capacitance (571.3 F g^{-1}) was obtained at 0.25 A g^{-1}. Besides, the specific capacitance of the composite electrode does not show a significant loss, indicating high cycle stability (93.02% after 1000 cycles). Based on all results, the authors stated that these outstanding electrochemical properties can be due to the presence of cobalt oxyhydroxide, which limits volumetric polypro replacement in the electrochemical redox process .[306]

4.2.3. Energy Storage Applications of Other Bio-renewable Resource-Based Nanocomposites

Today, the extinction of fossil fuel-based energy resources has increased and so is the importance of fuel cell applications. In particular, the design and energy efficiency of batteries that fuel cell-powered cars can use has been studied quite often in the transportation and automotive industries. Hydrogen storage materials have begun to attract interest in the production of fuel cell vehicles working with H_2 as a transportation alternative in recent years. However, the most important innovative approaches in this field are to design membranes which may pose a higher potential difference and new materials for storing hydrogen as fuel in fuel cells. In hydrogen storage applications, metal alloys such as Mg_2Ni, TiFe, $LaNi_5$, and $ZrMn_2$ are located in nanocomposite structures. Lei et al. [307] synthesized Mg-Ni/C nanocomposites for storing H_2. They used Vitamin C, which is a bio-renewable resource, as carbon source and Mg_2Ni and $Mg\text{-}Ni_2$ as metal alloys. The prepared structures had been characterized by several analysis techniques. XRD results had shown the formation of nanocomposite forms of Mg_2Ni and $Mg\text{-}Ni_2$ alloys with C. As a result, it had been reported by the study team that Mg-Ni/C nanocomposites would be the new nanocomposite materials in applications such as H_2 storage, electrocatalysts, optical switching, and gas adsorption.

Graphene/silk fibroin-based carbon nanocomposites (GCN-S) were prepared by Wang et al. [308] to develop high-performance supercapacitor. The obtained GCN-S materials had shown a high specific area, very good electrochemical performance, multi porous structure, and high electrical conductivity. For example, the specific capacitance value of GCN-S-0.5 material at the current density of 0.5 A/g had been measured as 256 F/g. Furthermore, when the current density increased to 50 A/g, the material had shown specific capacitance property at 188 F/g. Furthermore, at the charge-discharge rate of 5 A/g after 10000 cycles, the capacitance retention rate of GCN-S-0.5 had shown such a high rate of electrochemical stability as 96.3%. These study results show that GCN-S material as a new nanocomposite could be used for supercapacitor applications due to its high performance and cheapness.

Sun et al. prepared hybrid supercapacitor materials by bio-renewable corn silks based on porous carbon and redox-active electrolytes (Figure 42). In this study, the prepared material showed high specific surface areas of 1764.8 m^2/g, the large specific capacitance of 358.0 F/g at 0.5 A/g, 67% of the capacitance retention at 20 A/g, and retained 99.2% of initial specific capacitance after even 5000 cycles. [309]

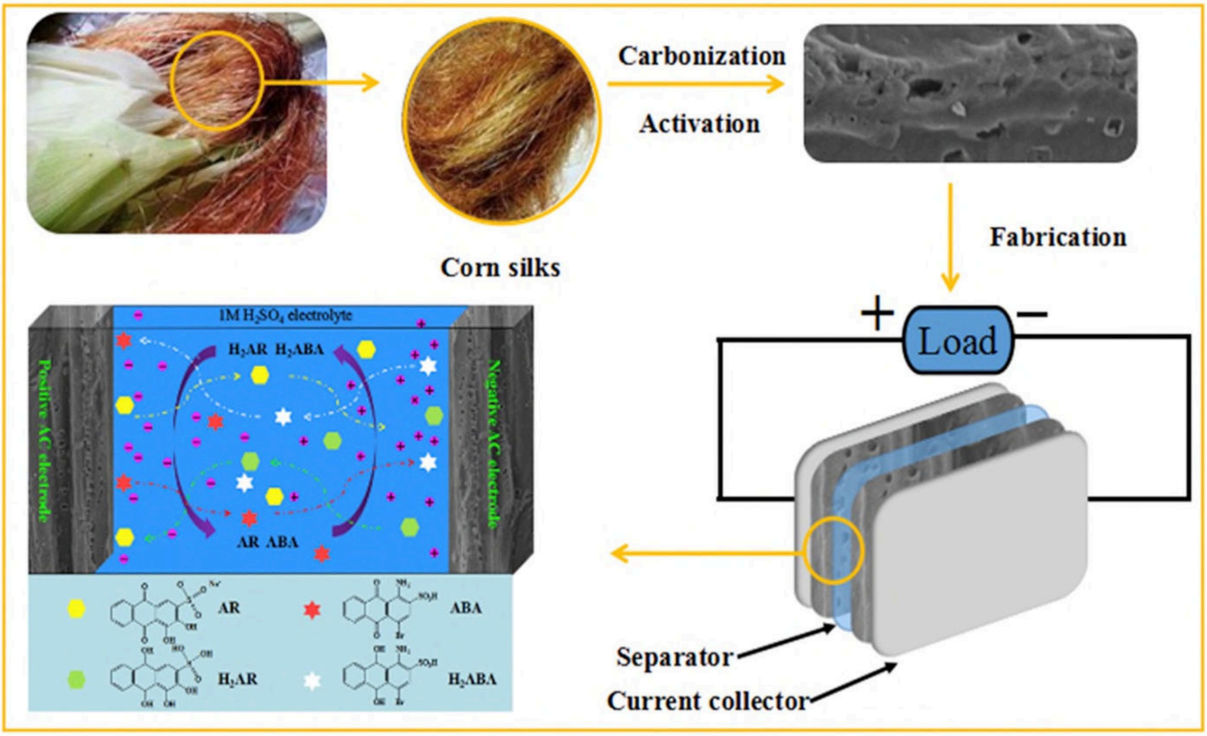


Figure 42. The general structure and working mechanism of the hybrid symmetric supercapacitor by bio-renewable corn silks based porous carbon and redox-active electrolytes**.** Reproduced with permission from ref [309]. Copyright 2018 Elsevier.

In a study of Bolisetty et al.[310], they first developed amyloid fibrils, an inorganic oxide (TiO_2), and π-conjugated polymers (polythiophene (P3HT)) based hybrid material capable of serving in heterojunction photovoltaic solar cell. To synthesize TiO_2–coated amyloid hybrid nanowires, protein fibrils act as templates to produce closely packed TiO_2 nanoparticles on the surface of the fibrils, while titanium (IV) bis (ammonium lactate) dihydroxide was used as a precursor. TiO_2 nanowires were found to behave as an electron acceptor, while P3HT as an electron donor. In this way, amyloid-TiO_2 hybrid nanowires can serve in photovoltaic devices. The C-V features of these photovoltaic devices displayed an outstanding fill factor of 0.53, the power conversion efficiency of 0.72% and the photovoltaic current density of 3.97 $mA.cm^{-2}$. The obtained results revealed that these photovoltaic devices may play a major role in amyloid-based templates in organic electronics, donor-acceptor devices and hybrid solar cells.

All these studies indicated that high technology products such as sensors, biosensors, batteries, energy storage systems, supercapacitor or solar panels can be prepared and applied from bio-renewable sources. In these areas, bio-renewable sources can be used as a film, foam, bulk material or coating material. Bio-renewable species have great potential in distributing or attaching important structures such as nanoparticles to a particular surface. Again, in sensor applications, they are of great importance in the bonding of electrocatalytic conductor types to the electrode surface as a selective film or membrane.

Samples of energy storage applications of nanocomposites from bio-renewable resources are also given in Table 6 as summary information.

Table 7. Energy storage applications of nanocomposites from bio-renewable resources

Composite	**Specific capacitance**	**Cycling performance**	**Density**	**Ref.**
MnO_2–CH	424 F g^{-1}	400 (97%)	1 mA cm^{-2}	290
CH-ZnO/PANI	587.15 F g^{-1}	1000 (80%)	175 mA cm^{-2}	291
CH/GM/PANI	609.2 F g^{-1}	500 (96%)	5 A g^{-1}	292
CH-graphene-PANI	1519 F g^{-1}	1000 (88%)	0.1 A g^{-1}	293
PPy/BC	459.5 F g^{-1}	100	0.16 A g^{-1}	301
N-doped rGO/C@Si	1077.4 mAh g^{-1}	150	4200 mA g^{-1}	295
N-doped carbon aerogels	185.3 F g^{-1}	5000 (90.2%)	0.5 A g^{-1}	304
NFC/PPy/TGCN	158 F g^{-1}	2000 (~91%)	5 mA cm^{-2}	305
PPy@cobalt oxyhydroxide/cellulose	571.3 F g^{-1}	1000 (93.02%)	0.2 A g^{-1}	306
Silk fibroin and graphene-based carbon (GCN-S)	256 F g^{-1}	10.000 (96.3%)	0.5 A g^{-1}	308

nitrogen doped biomass activated carbon	358.0 F g^{-1}	1000	0.5 A g^{-1}	309

5. Chemistry, Structure and Packing Applications of Nanocomposites from Bio-Renewable Resources

Plastics are the most widely used packaging materials because of their superior mechanical, thermal and physical behaviors. The packaging is one of the largest plastics markets in Europe. The main advantages of plastics are that they are cheap, lightweight, have high transparency, good processability and clarity, good barrier properties in terms of water vapor and gases compared to other packaging materials. However, the vast usage of plastics comes with environmental problems. The plastic packaging industry consists mainly of disposable products and is usually produced by oil. Therefore, it is necessary to use more environmentally friendly products to decrease the negative impacts on our environment and to make the packaging industry green.

Green packaging includes reusable packaging, degradable packaging, and packaging with recycled content. Polymer nanocomposites have great advantages because of their physical, thermal, mechanical and processing properties. Polymer nanocomposites used in packaging technology both improve the properties of polymer materials and provide additional functions for packaging. Nanoclay is one of the most used and researched nanofillers among polymer nanocomposites. Besides, nanoclay improves the mechanical and thermal properties of the material, the barrier properties to chemical vapors, moisture, gases, flavors, and solvents. The inclusion of nanoclay to the high-density polyethylene (HDPE)/rice husk improved its tensile strength, storage modulus, tensile modulus and loss modulus. [311] Compositions of nanoclay containing 2 phc (parts per hundred content) were found to have the best morphology as nested structures among other composites. Moreover, crystallization temperature, crystallinity level and crystallization enthalpy of HDPE/rice husk increased because of nanoclay. The author proposed that a fully dispersed morphology could be achieved by increasing the compatibilizer load.

The mechanical properties and water absorption properties of nano silicon carbide-filled recycled cellulose **fibre** (RCF)-reinforced epoxy econanocomposites had been reported by Alamri and Low. [312]

It is believed that nanofillers high aspect ratio increases the barrier performance of the materials by generating tortuous ways to diffuse into the composites of water molecules. The maximum water uptake of RCF/epoxy composites containing 5%w n-SiC decreased with 47.5% compared with without filling.

Bio-renewable resources based polymers such as vegetable oils and fats, corn starch or pea starch are commonly called biopolymers. Furthermore, some biopolymers may also be produced as biodegradable, which may be degraded by other living organisms or bacteria. Most biodegradable polymers are generally designed to be compostable. PLA, S, and polyhydroxy butyrate (PHB) are typical biodegradable biopolymers from bio-renewable resources. There are many reports about nanofillers reinforced biopolymers. Although pure biopolymers have high hydrophilicity, poor processability, and poor mechanical properties, nanofillers reinforcements increase the mechanical and thermal properties of the material. [313–315] Wu et al. [316] showed the graft polymerization of PLA on the surface of nano-SiO_2 and investigated the properties of PLA/PLA-grafted SiO_2 nanocomposites. It was observed that PLA-grafted SiO_2 could hasten the crystallization rate and enhance the PLA's degree of crystallinity. The shear rheology test demonstrated that PLA/PLA-grafted SiO_2 nanocomposites displayed the typical homopolymer-like behavior in the final structure, even in the low-frequency range, even at a SiO_2 content of

5% by weight of PLA grafted. Li and Sun [317] fabricated PLA/g-MgO nanocomposites via thermal compounding of g-MgO/MgO nanoparticles and PLA. It was observed that PLA/g-MgO nanocomposites showed improved thermal stability and higher tensile strength in comparison to the pristine PLA and PLA/g-MgO nanocomposites. Polymer foams are commonly used since they are very significant as packaging materials. They protect the products with controllable performance. Generally, important properties of polymer foams are dimensional and thermal stability, surface quality, and mechanical properties including force and shock absorption. The integration of the nanofillers into the polymer foam improves the performance of the foams for the packaging materials.

In another study, Sanchez-Garcia et al. [318] determined the association between barrier and morphology properties of PHB/clay nanocomposites. They found that the nanoclay exhibited a great dispersion in the PHB matrix owing to the clay modification. Besides, they reported that the high dispersion caused improvement in the water and oxygen barrier properties of PHB/clay nanocomposites.

In 2015, Salaberria et al. [319] explored the effect of nanochitins of different morphology on the functional and structural properties of thermoplastic starch-based films manufactured by the evaporation casting method. The barrier properties of the S matrix were significantly influenced by both the chitin nanocrystals (CHNC) and the chitin nanofibres (CHNF) and their quantity. For nanocomposite films prepared with CHNC and CHNF, the oxygen permeability of the thermoplastic starch-based matrix decreased by 30% and 25%, respectively. Considering the water vapor permeability, water vapor transmission values were reduced in the presence of up to 10 percent by weight of the CHNC. Poor barrier properties were founded beyond this concentration. There are two reasons for these findings. One is the presence of excess residual amino groups on the surface of the chitin nanomaterials, which exhibit greater affinity for water than hydroxyl groups. Another reason is the occurrence of agglomeration events induced by an excessive amount of CHNC or CHNF content. The effective chitin in the matrix can reduce the amount of nano-injection, which indicates the barrier effects (Figure 43).

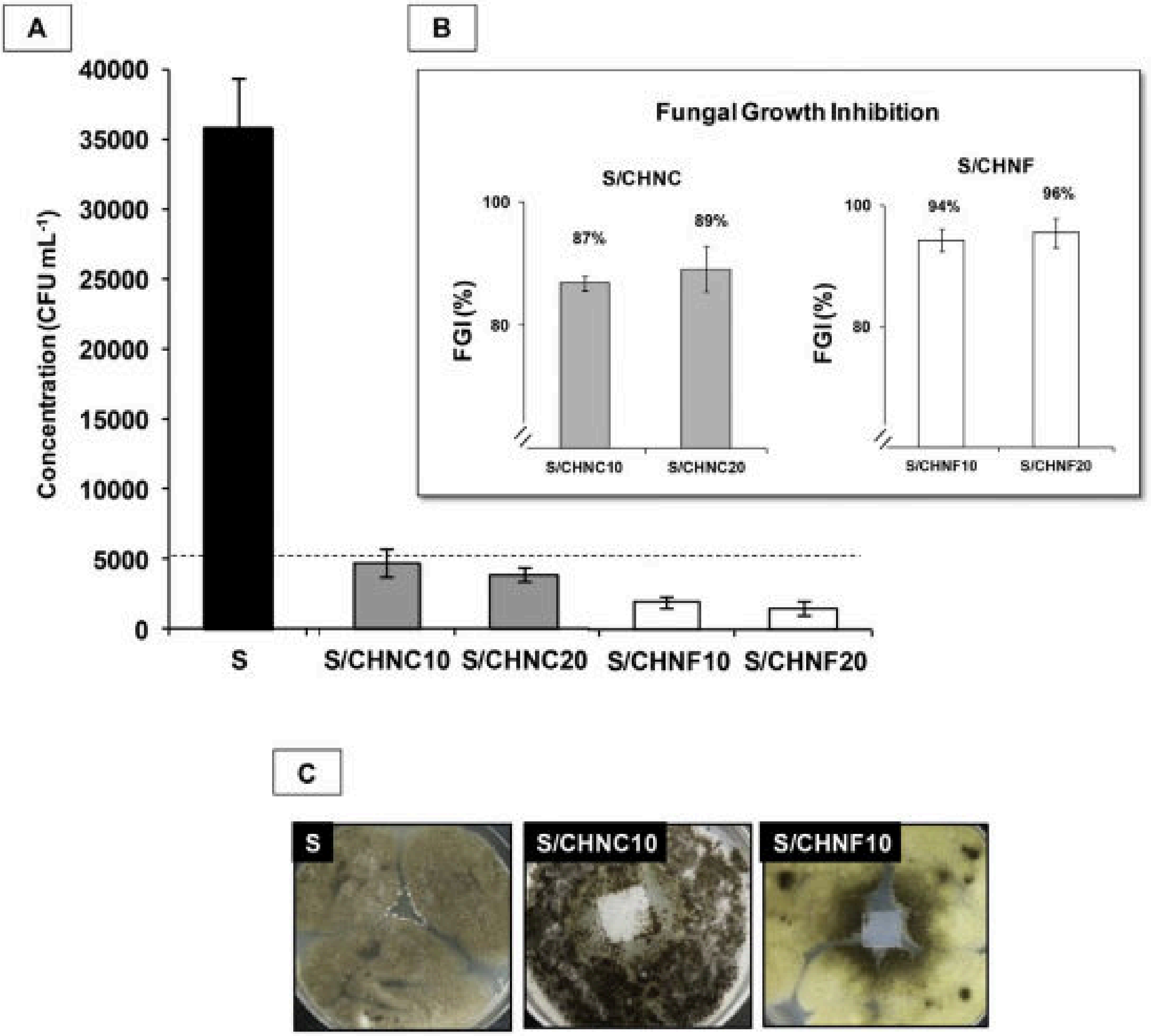


Figure 43. A. Effect of starch film, and CHNC and CHNF nanocomposite films on the growth of *Aspergillus niger*; B. Fungal Growth Inhibition (FGI, %) on the growth of *Aspergillus niger* on S/CHNC and S/CHNF for 10 and 20% of chitin nano-objects (error bar corresponds to standard deviation: SD, n=3); and C. Pictures of the agar plates containing *Aspergillus niger* in contact with the square films of S, CHNC10, and CHNF10 (7 days for contact time). Reproduced with permission from ref [319]. Copyright 2015 Elsevier.

Nafchi et al. [320] produced bovine gelatin and sago starch nanocomposite films containing ZnO nanorods (1–5 wt.%). All the prepared films were plasticized with 40% (w/w of total solid) of a combination of sorbitol/glycerol (3:1 ratio). The barrier properties of the biopolymer matrix were improved due to the ZnO nanorods. The oxygen permeability of starch and gelatin films containing 5% of ZnO nanorods were reduced by 40% and 55%, respectively.

Bhat and his colleagues [321] improved the poor barrier and mechanical properties of starch-based films with the incorporation of different weight percent of lignin (1–5 wt.%). A significant reduction (~35%) was observed in the water vapor permeability of composite materials containing 1% or 2% by weight. The authors reported that this reduction was due to the compatibility and hydrophobicity of the combinations of starch and lignin, which cause the water vapor of the diffusion to fall between the films.

Dash and Swain [322] had used nano silicon carbide up to ten weight percent loadings for preparing starch-based composites. The oxygen permeability of the biopolymer matrix containing the highest nanofillers concentration was found to be reduced by 3.5 times (Figure 44).

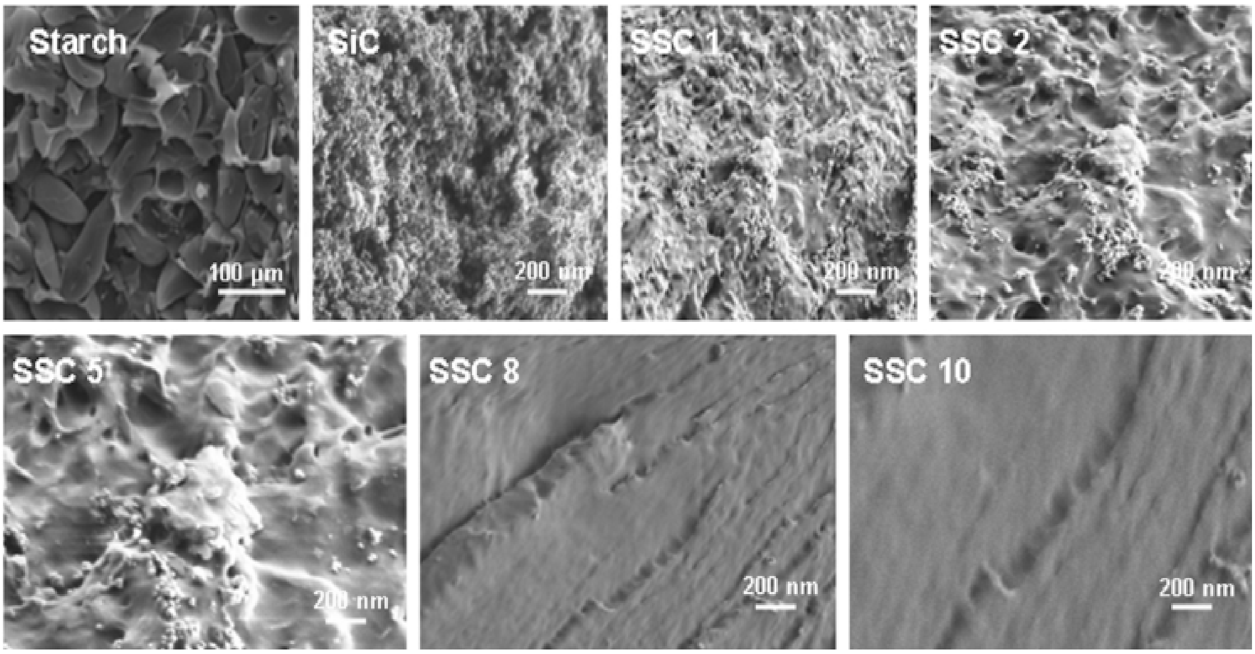


Figure 44. FE-SEM images of S, silicon carbide (SiC) and S/SiC bionanocomposite at a different weight percent of SiC (SSC1, SSC2, SSC5, SSC8 and SSC10). Reproduced with permission from ref [322]. Copyright 2013 Elsevier.

Dash et al. [323] produced albumin bovine based bionanocomposite containing different amounts of organoclay (1, 2, 5, 8 and 10 percent of weight). The oxygen barrier properties of the resulting nanocomposites were determined and the reduction in the permeability of the sample containing 10% by weight of clay was observed. This reduction is due to the intercalation of albumin bovine into the clay.

In 2012, Luduena et al. [324] prepared PCL-based biodegradable composites containing different types and amount of lignocellulosic for packaging applications and examined the effects of these fillers on the morphology, mechanical, crystallization behavior and thermal, and barrier properties. Moreover, the barrier properties of the prepared materials were investigated. However, in contrast to the type of lignocellulosic filler used, it was found that the water vapor permeability values increased by increasing the filler amount due to the tendency of the fillers to agglomerate.

Follain et al. [325] fabricated PCL/CNC based nanocomposite films via a film casting/evaporation technique. The effect of CNC (3-12%) by weight on the barrier properties of PCL was evaluated using water absorption/passing processes. According to the obtained results, the rod-like morphology of the CNC reduces water permeability as it extends the diffusion path of the molecules emitted due to tortuosity structure.

Swain et al. [326] prepared a series of soy protein nanocomposites containing Cloisite 30B (one to eight percent by weight) via a solution intercalation technique. In their study, it was found that oxygen permeability of nanocomposite samples containing 8% nanoclay decreased 6-fold compared with unfilled one.

In 2011, Rhim and his colleagues [327] fabricated agar-based nanocomposite films containing several nanoclay samples (Cloisite 20A, Cloisite Na^+, and Cloisite 30B) through a solvent casting technique. The water vapor permeability of the fabricated materials was found to be dependent on the kind of nanoclay in comparison to the unloaded agar films. For instance, the nanocomposite films containing Cloisite Na^+ indicated low water vapor permeability, unlike the films that contain the organically modified nanoclay because of the surface hydrophilicity/hydrophobicity of the used clays.

Gonzalez and Alvarez Igarzabal [328] prepared starch nanocrystals reinforced soy protein isolate films in which the amounts of nanocrystals was varied from 0, 2, 5, 10, 20 and 40 w/w using a facile casting technique. The inclusion of the nanofillers has caused swelling of the protein film as well as lowering the water vapor permeability (Figure 45).

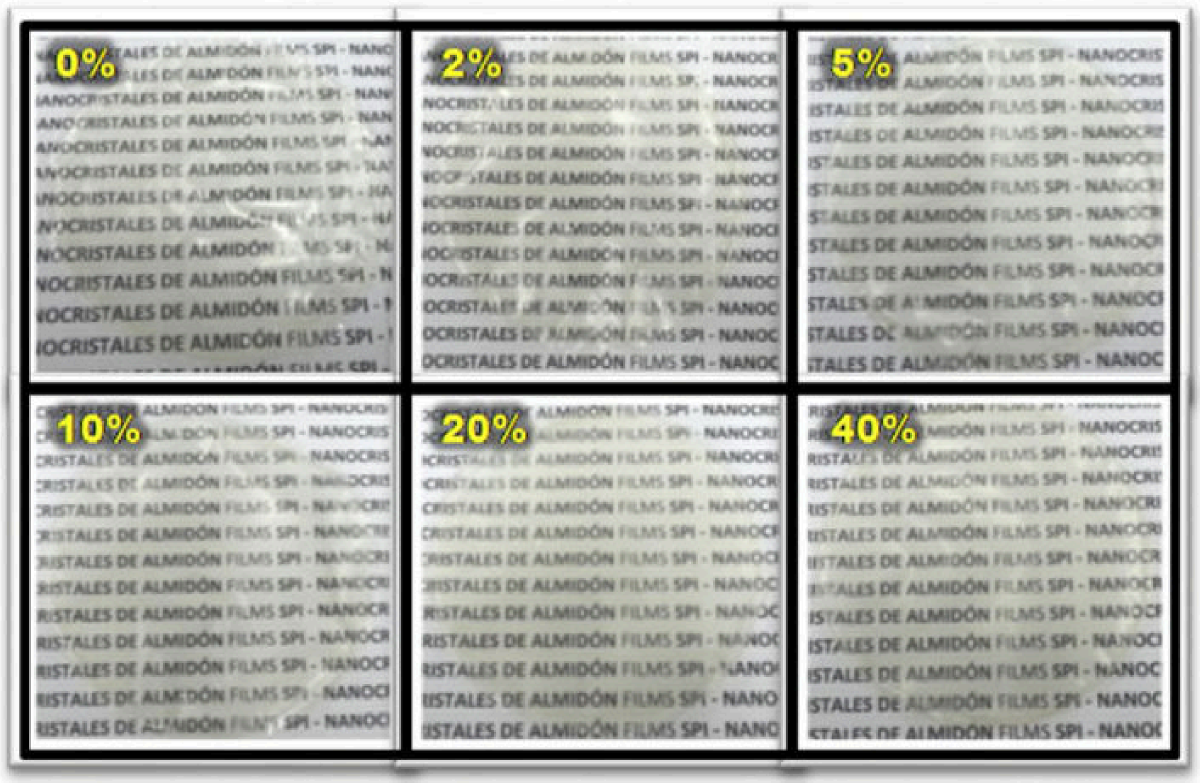


Figure 45. The macroscopic aspect of soy protein isolates films with 0, 2, 5, 10, 20 and 40% w/w of starch nanocrystals. Reproduced with permission from ref [328]. Copyright 2015 Elsevier.

Kumar et al. [329] used the melt extrusion method to obtain bionanocomposite films containing soy protein isolate and different contents of montmorillonite, Cloisite Na^+ (5-15 wt.%). The nanoclay was used to significantly reduce the water vapor permeability. Only, for the film containing 5 wt.% of MMT, the water vapor permeability was reduced by 22.1%. “This decrease was because of the creation of a tortuous pathway for water vapor to diffuse out of the bionanocomposite”. Besides, the other reasons could be the homogeneous distribution and high aspect ratio of the employed nanoclay.

In 2013, Abdollahi et al. [330] applied a solvent casting method for production of alginate-based nanocomposites containing montmorillonite and cellulose nanoparticles. It was found that both nanofillers having concentrations ranging from 1 to 5 wt.% significantly changed the water solubility. The water vapor permeability's of the prepared material was reduced by 18% and 20% in alginate/cellulose and alginate/montmorillonite nanoparticles, respectively.

Kochumalayil et al. [331] produced bionanocomposite coatings based on montmorillonite (Cloisite Na^+) and xyloglucan also known as galactoxyloglucan. They used continuous water-based processing method and obtained coatings at different ratios of 4.3, 8.9 and 20 wt.% (Figure 46). It was revealed that the biopolymer matrix containing the highest nano-layer is very efficient for oxygen permeability, which makes the bio-nano compound a promising material in the packaging industry rather than aluminum gas barrier films (Figure 47).

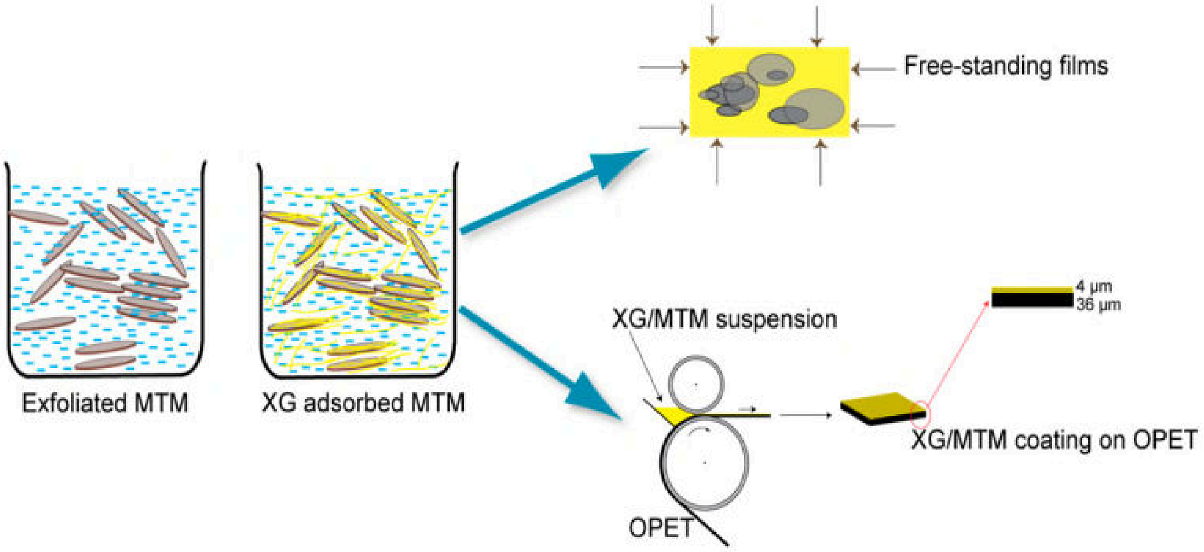


Figure 46. The preparation procedures of xyloglucan (XG)/MTM nanocomposite film. Reproduced with permission from ref [331]. Copyright 2013 American Chemical Society.

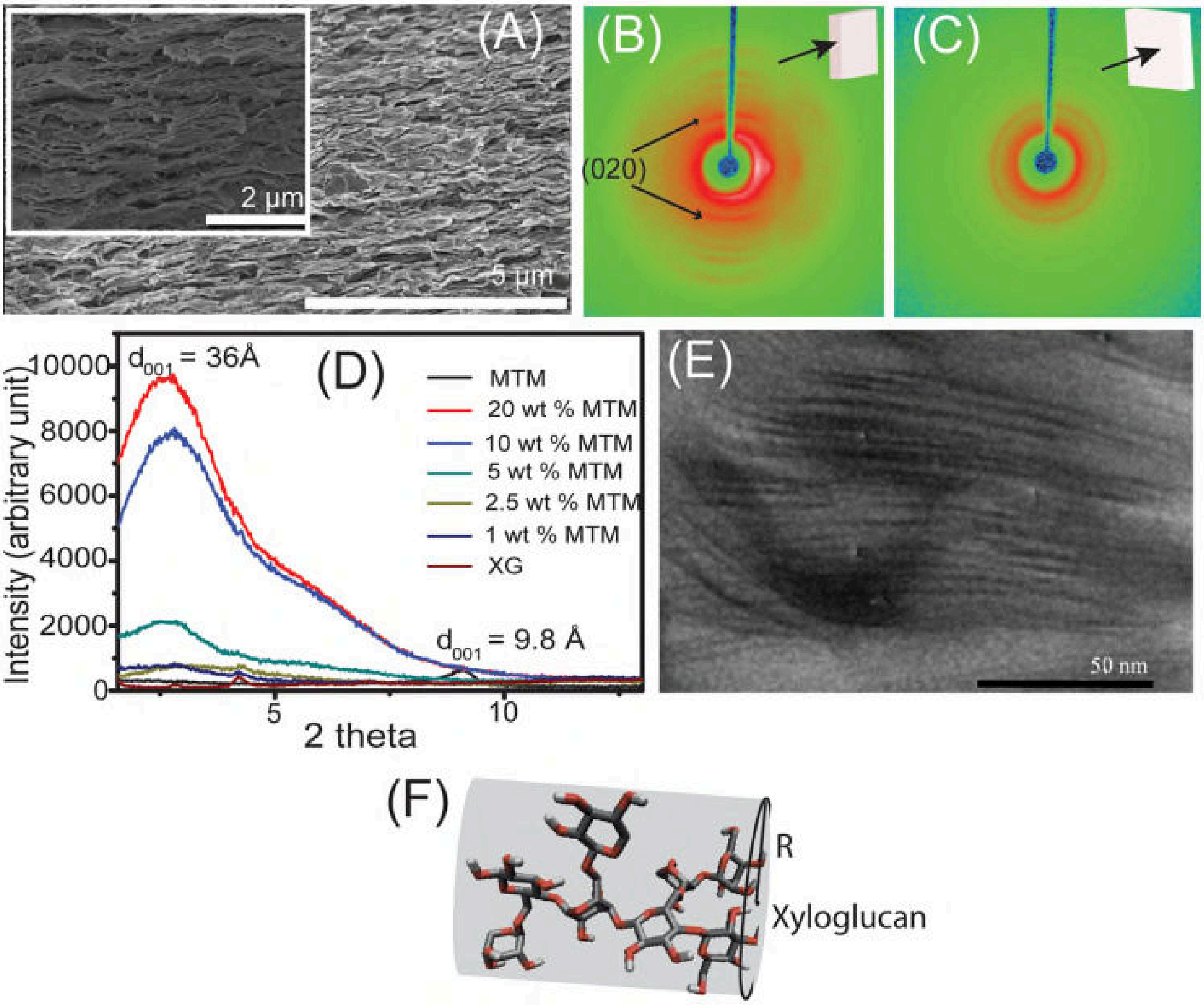


Figure 47. (A) The cross-sectional SEM micrograph of a nanocomposite containing 10 wt% MTM in xyloglucan (XG) matrix and X-ray diffractograms of a nanocomposite film containing 20 wt% MTM in parallel (B) and perpendicular (C) to the film surface. (D) XRD pattern of the XG-MTM hybrid material. (E) A TEM micrograph of the cross-section of XG-MTM nanocomposite containing 10 wt% of MTM showing the silicate layers as alternating dark lines. (F) The schematic image of an XG chain fragment modeled as a cylinder. R is the XG radius. Reproduced with permission from ref [331]. Copyright 2013 American Chemical Society.

The low-cost packaging materials are no longer having the most popular advantages concerning the deterioration of the environment and fast-depleting resources. Polymer nanocomposites from bio-renewable resources have valuable functions and advanced physical, thermal and mechanical properties. Therefore, biodegradable polymers are an excellent candidate as a matrix in green packaging.

Samples of the packing applications of nanocomposites from bio-renewable resources are also given in Table 8 as a piece of summary information.

Table 8. Packing applications of nanocomposites from bio-renewable resources

Composite	**Barrier property**	**Density, ρ (g/cm^3)**	**Permeability**	**Tensile strength (MPa)**	**Ref.**
PHB/clay nanocomposites	O_2	ρ_{PHB}: 1.25 ρ_{PCL}: 1.1	PHB-Blend: 4.2 ± 0.0005 e^{-19} 1% Nanoter PHB-Blend: 3.8 ± 0.3 e^{-19} 4% Nanoter PHB-Blend: 2.4 ± 0.3 e^{-19} PHB: 2.3 ± 0.002 e^{-19} 4% Nanoter PHB: 1.8±0.3 e^{-19} PCL: 58.0 e^{-19} PET: 3.3 e^{-19} [cc.μm/(m^2.day) kPa^{-1}] (at 24°C, 0% RH)	-	318
S matrix with CHNC or CHNF	O_2	-	S/CHNC: 30% decreased compared to S film S/CHNF: 25% decreased compared to S film (at 23 ± 2°C, 75% RH)	S/5 wt% CHNC: 2 S/20 wt% CHNC: 3	319
Sago starch and bovine gelatin bionanocomposite films containing ZnO nanorods (1–5 wt.%)	O_2	-	Sago starch 0% ZnO nanorods: 79.88 ± 2.44 1% ZnO nanorods: 68.72 ± 1.28 2% ZnO nanorods: 56.98 ± 1.02 3% ZnO nanorods: 53.77 ± 0.50 5% ZnO nanorods: 48.20 ± 0.81 Gelatin	Sago starch 0% ZnO nanorods: 3.47 ± 0.34 1% ZnO nanorods: 5.19 ± 0.49 2% ZnO nanorods: 5.31 ± 0.32 3% ZnO nanorods: 5.45 ± 0.25 5% ZnO nanorods: 6.62 ± 1.02 Gelatin	320

			0% ZnO nanorods: 226.18 ± 7.92 1% ZnO nanorods: 207.94 ± 7.34 2% ZnO nanorods: 154.54 ± 3.75 3% ZnO nanorods: 136.31 ± 3.60 5% ZnO nanorods: 104.59 ± 6.14 [cm^3.µm/ (m^2 day.atm)] (at 25°C, 50% RH with 21% O$_2$)	0% ZnO nanorods: 15.63 ± 0.74 1% ZnO nanorods: 17.07 ± 0.69 2% ZnO nanorods: 18.71 ± 0.85 3% ZnO nanorods: 19.39 ± 1.09 5% ZnO nanorods: 21.13 ± 1.52	
Starch-based films with the incorporation of different weight percent of lignin as 1–5 wt.%	Water vapor	-	Control film: 0.017 1 wt% isolated lignin films: 0.011 ± 0.001 2 wt% isolated lignin films: 0.012 ± 0.001 (g.mm/m^2. h. kPa) (at 30°C, 58% RH)	1 wt% isolated lignin films: 3.48 ± 0.15 2 wt% isolated lignin films: 3.76 ± 0.40 3 wt% isolated lignin films: 4.20 ± 0.42	321
PCL-based biodegradable composites containing different types and amount lignocellulose	Water vapor	ρ_{PCL}: 1.2	PCL: 1.6 ± 0.1 5 wt% cotton: 2.0 ± 0.1 15 wt% cotton: 2.3 ± 0.1 5 wt% cellulose: 1.6 ± 0.1 15 wt% cellulose: 1.7 ± 0.2 5 wt% hydrolyzed-cellulose: 1.9 ± 0.2 15 wt% hydrolyzed-cellulose: 2.0 ± 0.4 (x 10^{-11} g.m/m^2. s. Pa) (at 25°C, 68% RH)	PCL: 19.0 ± 0.5 5 wt% cotton: 16.2 ± 0.3 15 wt% cotton: 14.2 ± 0.3 5 wt% cellulose: 19.0 ± 0.7 15 wt% cellulose: 19.4 ± 0.9 5 wt% hydrolyzed-cellulose: 17.6 ± 0.5 15 wt% hydrolyzed-cellulose: 12.1 ± 0.7	324
Agar-based nanocomposite films containing several nanoclay samples	Water vapor	-	Neat agar film: 2.22 ± 0.19 Agar/Cloisite Na$^+$: 1.68 ± 0.24 Agar/Cloisite 30B: 2.31 ± 0.14 Agar/Cloisite 20A: 2.62 ± 0.18 (x 10^{-9} g.m/m^2. s. Pa) (at 25°C, 50% RH)	Neat agar film: 29.7 ± 1.7 Agar/Cloisite Na$^+$: 35.0 ± 2.1 Agar/Cloisite 30B: 28.6 ± 1.0 Agar/Cloisite 20A: 29.3 ± 0.9	327

Soy protein isolate (SPI) films with starch nanocrystals	Water vapor	-	SPI: 4.3 ± 0.2 SPI-5% starch nanocrystals: 4.8 ± 0.3 SPI-20% starch nanocrystals: 3.9 ± 0.1 SPI-40% starch nanocrystals: 3.57 ± 0.08 (x 10^{-10} g/m.s. Pa) (at 25°C, 65% RH)	SPI: 1.10 ± 0.20 SPI-2% starch nanocrystals: 1.42 ± 0.22 SPI-5% starch nanocrystals: 1.34 ± 0.07 SPI-10% starch nanocrystals: 1.79 ± 0.27 SPI-20% starch nanocrystals: 2.61 ± 0.26 SPI-40% starch nanocrystals: 5.08 ± 0.48	328
Bionanocomposite films containing soy protein isolate (SPI) and different contents from 5 to 15 wt % of montmorillonite, Cloisite Na$^+$	Water vapor	ρ_{MTM}: 2.86	SPI: 3.80 ± 0.11 SPI-5% MMT: 2.96 ± 0.10 SPI-10% MMT: 2.49 ± 0.08 SPI-15% MMT: 2.17 ± 0.06 (g.mm/m^2. h. kPa) (at 22°C, 65% RH)	SPI: 2.26 ± 0.48 SPI-5% MMT: 6.28 ± 0.88 SPI-10% MMT: 12.62 ± 0.54 SPI-15% MMT: 15.60 ± 1.69	329
Alginate-based nanocomposites containing 5% montmorillonite and cellulose nanoparticles	Water vapor	0.600	Control film: 1.99 ± 0.19 x 10^{-10} g/m^2. s. Pa Nanocomposite with 5% MMT: ~20% decrease Nanocomposite with cellulose nanoparticles: ~18% decrease (at 20°C, 1.5% RH)	18.03	330
Bionanocomposite coatings based on montmorillonite (Cloisite Na$^+$) and xyloglucan	O_2	ρ_{XG}: 1.5 ρ_{MTM}: 2.86	XG: 0.45 ± 0.00 XG + 4.3 wt % MMT: 0.18 ± 0.009 XG + 8.9 wt % MMT: 0.04 ± 0.001 XG + 20 wt % MMT: 0.05 ± 0.000	XG: 92.9 ± 5.8 XG/1 wt % MTM: 89.1 ± 6.9 XG/2.5 wt % MTM: 96.2 ± 6.7 XG/5 wt % MTM: 103.9 ± 2.7	331

	$[cc.\mu m/(m^2.day)\ kPa^{-1}]$ (at 23°C, 50% RH)	XG/10 wt % MTM: 114.3 ± 6.3 XG/20 wt % MTM: 123 ± 7.4 (at 23°C, 50% RH)

6. Chemistry, Structure and Optical Applications of Nanocomposites from Bio-Renewable Resources

Recently, nanocomposites have received a greater interest because they have shown a pronounced potential to be used in several applications ranging from light-emitting diodes, solar cells, light filters, light-stable color filters, optical sensors, optic data communications, and optical data storage to name a few. Since nanocomposites are prepared from two or more different materials that have distinct mechanical, electronic and chemical characteristics, they have particular importance in selected applications. [332] Nanocomposite structures provide a new method to improve the workability and stability of materials possessing interesting optical properties. [333] Recently, bio-nano composites having a low cost, renewable, biocompatible and environmental (green) processes have seen the upsurge in research and industry. Different kinds of nanocomposite structures have been synthesized using bio-renewable resources such as CH, cellulose, lignin, gelatin as the main ingredient or matrix materials and the optical properties of these structures have been examined in detail.

CH, consisting of *N*-acetyl-D-glucosamine and β-(1-4)-D-glucosamine, is the most popular candidate used in optical applications because of being a natural, biocompatible, biodegradable and non-toxic polymer, and capable of forming a superior film. [334] Furthermore, since CH has both hydroxyl and amino functional groups, bioconjugates can be prepared with various chemical modifications of proteins, DNA and other polysaccharides. [335–337] In nanocomposite structures, CH is widely used in several biotechnological applications due to its above-mentioned characteristics.

Bozanic et al. [338] prepared Ag-CH nanocomposites using in situ green chemistry methods and D-glucose as reducing agent from Ag-CH complexes. The synthesized nanocomposites had been characterized with TEM, UV-Vis, FT-IR, and photoluminescence spectroscopy and the optical properties were examined in detail. Especially, Ag-CH complexes doped with different amounts of Ag had shown different electronic properties due to the complexation of silver with CH chains. In particular, three different peaks had been seen from the UV spectrum of these complexes. The peaks seen at 376, 467 and 562 nm had grown with the increasing amount of Ag in a complex structure. The absorption band at 376 nm had taken place with an energy of 3.3 eV, whereas the absorption at 467 nm had required 2.7 eV energy. Finally, the absorption band observed at 562 nm was due to the formation of individual silver nanoparticles. This variable spectrum of the obtained optical film at 390 nm had led to show fluorescence properties with a strong emission band. In conclusion, this study had demonstrated that AgNPs such as Ag, AgO, AgI, and Ag_2S have important material characteristics in the preparation of semiconductor devices.

Mironenko et al. [339] used CH-Ag particles in electronic systems as a waveguide. They showed that the raised refractive index with increasing silver content in the film structure of such nanocomposites might be used as suitable surfaces in the preparation of many optical sensors.

In the preparation of significant optical materials, another important ingredient derived from bio-renewable resources is herbal and BC using as matrix material. Cellulose, which is a bio-renewable resource, is quite important in the design of optical materials as a matrix and a reinforcement. They had been used especially in semiconductors such as CdS-ZnS, ZnS-CdS, and CdS, ZnS, and this type of photoluminescence specific reinforcements into the cellulose matrix.

Hassan et al. [340] achieved strong optical emission peaks at 450 nm using semiconductors obtained from CdS doped cellulose nanocomposites. Besides, they had shown that many optical materials could be prepared with the strong dielectric property provided in such nanocomposites.

In another similar study, Zheng et al. [341] achieved optical materials having a semiconductor feature with the application of ZnS nanoparticles into BC. These materials had shown two emission peaks at 424 and 468 nm and had been proposed as nanocomposite having strong fluorescence properties.

Cellulose matrix nanocomposites had been preferred in certain medical and sensor applications not only as semiconductors but also as transparent films due to their low environmental impact and biodegradability. Hambardzumyan et al. [342] achieved 100% permeable surfaces prepared in different rates of cellulose-lignin films. They showed that both the transparent and the antireflective properties of the material were achieved in the coating of these surfaces with diverse layers especially in the ranges from 300 to 800 nm.

Cellulose **fibre**s had also been used in optical materials as a reinforcement obtained directly from natural resources (Figure 48). Nanocrystalline doped into the polyurethane matrix had increased the mechanical properties of cellulose polyurethane structure but it had caused a reduction in optical properties. [343] Although the nanocomposites prepared with cellulose doping in polylactic acid had shown 84% of optical transmittance, they exhibited very high mechanical properties. In the study, Herrera et al. [344] reported that mechanical strength would be increased without compromising the optical properties of polylactic acid.

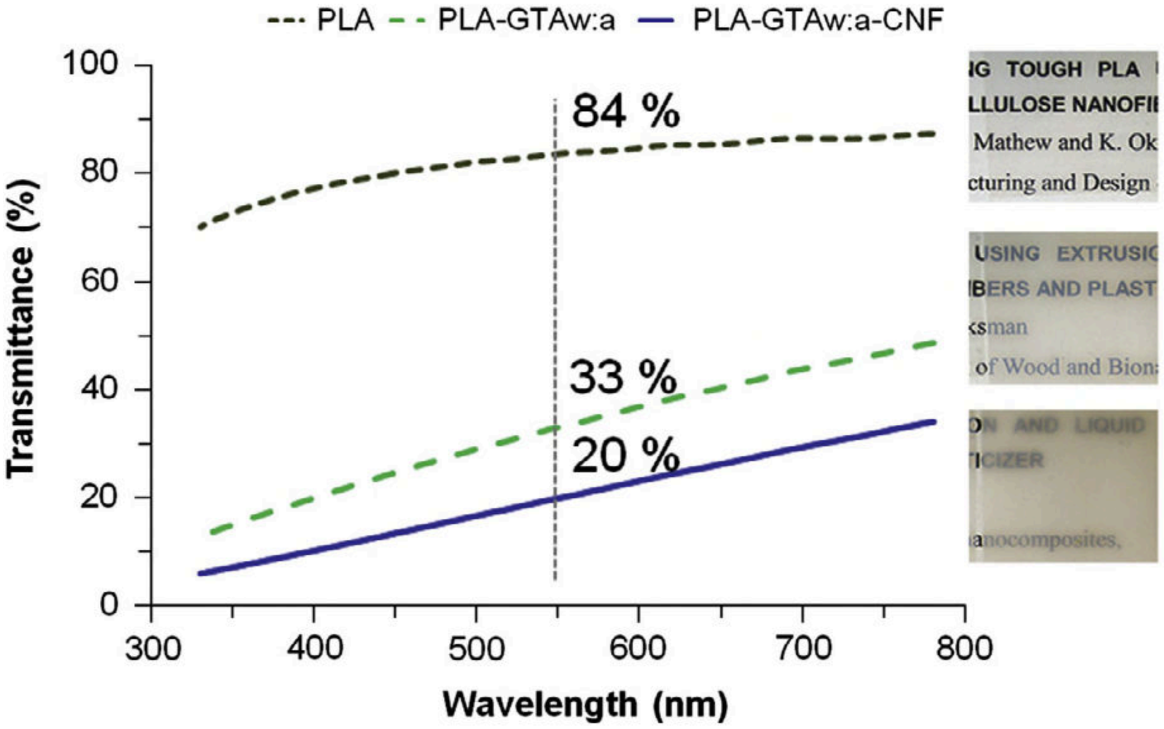


Figure 48. Transmittance (%) levels and transparency of the films. Reproduced with permission from ref [344]. Copyright 2015 Elsevier.

When organo-modified clay was doped into PLA (a bio-renewable and environmentally friendly resource, derived from lactic acid), the optical transmission of the system was found to be around 85% despite the 7% of clay inclusion. Clay doped nanoparticles have shown the stable surface morphology and surface reflectance, however, the optical transmittance of the film was found to be affected. [345]

All of these results indicate that many materials and surface films which can be used in biomedical, electronic and optoelectronic systems can be obtained with doping of nanoparticles having different features from renewable natural resources. Although such films have low mechanical and chemical stabilities, they are capable of competing with petrol-based polymers because of their optical, electrical, and dielectric properties. Using reinforcements and pure nanoparticles to strengthen the weak characteristics or to impart new properties of the natural polymers, carbon nanotube metal oxides are highly popular in contemporary daily applications. [346]

In the study of Mahmoud et al. [347] transparent dressing films for wounds that can be used in cosmetics and biomedical applications had been prepared from an easily deformable renewable resource such as gelatin with silver particles doped into the pure gelatin. With increasing the amount of silver up to 1%, properties such as refractive index and dielectric constant had been examined. In these films, the gelatin structure had been reinforced and an antibacterial surface had been obtained in wound healing dressings.

7. Chemistry, Structure and Automotive Applications of Nanocomposites from Bio-Renewable Resources

Nanocomposites originated from bio-renewable resources have widely gained importance in automotive applications as sustainable alternatives to petroleum-based polymers. Especially, petroleum-based polymers have lots of environmental problems such as increasing greenhouse gas emissions, and water pollution as well as exceeding the current capacity of solid-waste management systems. Since bio-renewable nanocomposites are biodegradable, the replacement of petroleum-based nanomaterials with these bio-renewable nanocomposites for example in the usage of disposable products has some advantages such as reducing not only solid waste but also release of carbon dioxide into the atmosphere. Nanocomposites from bio-renewable resources are neutral in terms of carbon releasing because their lives finish via biodegradation with the carbon cycle, which means that the release of carbon dioxide related to these products is taken by plants and given back to the atmosphere as continuously occurring natural phenomena. [348] Besides, the automotive industry is an extremely user of bulk materials such as steel and plastics during the production of a vehicle. In the near future, most cars manufactured from nanocomposites using bio-renewable resources will be a good resource of recyclable materials. Approximately eighty percent of a car can be recycled today. [349] Unfortunately, heavy composites used today in the structure of any vehicle importantly influence the fuel consumption as well. Thus, researchers in the automotive industry are trying to increase this ratio and improve lightweight and strong nanocomposites from bio-renewable resources day-by-day.

In general, both natural fibre and biopolymers from green nanocomposites lower processability and mechanical properties and increase some characteristics such as hydrophilicity and moisture absorbance. Particularly in the exterior automotive components, these disadvantages restrict their applications. To be applied in the automotive industry, researches and developments are needed to overcome these problems in the composites, which are ecological, lightweight and economic. To enhance the performance of these nanocomposites, use of nanofillers is among one of the best approaches. Chieng et al. [350] investigated the elongation and tensile strength at the disruption of epoxidized palm oil/poly(lactic acid) and found an increase of 60.6 %, and 26.5 % with 0.3 wt.% of nano-graphene, respectively. In another study, Nemati et al. [351] researched wood-plastic composites obtained from nanoclay, wood flour and recycled polystyrene in terms of the mechanical properties. The lignin and natural fibre nanocomposites contained in either organically modified nanoclay or sepiolite were prepared [352]. It had been observed that the addition of 2-5 % w/w of sepiolite did not affect the thermal and mechanical properties of the natural fibre nanocomposites. On the other hand, nanoclay-based nanocomposites were found to show enhanced properties.

To prevent the dispersion of volatile products from thermal degradation of composites, the nanoscale clay layers have been used as an inert barrier. For example, nanocomposites were prepared from natural fibres, lignin and natural reinforcements. The prepared nanocomposites had demonstrated similar mechanical properties related to those of polyamides. However, in automotive applications, the fire resistance and thermal stability of the nanocomposites should be further improved. Principally, the addition of suitable compatibilizer is estimated to improve the miscibility of clay nanofillers and composite matrix. In the near future, these nanocomposites may replace petroleum-based polymer plastics in automotive applications.

8. Chemistry, Structure and Flame Retardancy Applications of Nanocomposites from Bio-Renewable Resources

Today, technology is rapidly increasing along with the need for increasing the performance of existing materials in human daily life. Therefore, it is very important to develop a new generation of high-performance materials. Since high-performance materials typically have strong secondary interactions and molecular structures, their chemical and thermal stability is very high. Besides such stabilizations, they are not biologically degradable because of their quite high biodetermination. After the usage, they are a prime cause of pollution because of being accumulated in nature. To prevent this contamination, renewable polymers that degrade in nature have been used. However, this situation has brought new problems. The foremost problem among these is that these polymers are not very resistant to thermal effects. One of the major disadvantages of such polymeric materials is that the resistance of the materials against burning namely flame-retarding property is extremely low. Nanocomposite technology has come to the fore to prevent this situation. Some metal oxides, clay species and the water releasing molecules at high temperatures are used as reinforcement to increase the flame resistance and thermal stability of these structures.

Renewably resourced bio-polymeric nanocomposites have come to the forefront in material science recently because of their superior properties. However, since such polymers have very high proportions of carbon, hydrogen and oxygen-containing compounds, they burn easily and quickly and during the burning of these polymers toxic and flammable gases as byproducts with heat are released. These gases are unsafe to human health at least the flames. Moreover, with the fragmentation of the polymer chains into small pieces or molecules by the effect of heat the medium becomes more flammable than the initial conditions. Therefore, researchers are exploring the use of flame retardant materials to prevent the burning of polymers in order to improve the performance of polymeric nanocomposite materials. The composite structure obtained from different reinforcements having flame retardant property gains flame retardancy and are achieving the security levels of applications that restrict the use of such polymers. [353] However, since these materials are very dangerous, it is much more prominent to develop efficient, cheap and environmentally friendly flame retardants. In various aspects, flame retardant reinforcements can be classified according to their basic mechanisms, targeting polymer types, containing an element or compound types. Flame retardants are the compounds having metal hydroxide compounds and one or more elements from phosphorus (P) or 7A group (halogen) according to the commonly used classification format.

PLA is widely used in biomedical materials, bags, packaging and films, fibres. Nevertheless, PLA is flammable like other polymers and this fact restricts the use of PLA in electric or electronic applications.[354] Therefore, nanocomposite structures have been prepared by the combination of different flame retardants with PLA, which is a renewable biopolymer. For instance, isopropylated triaryl phosphate ester known for flame retardant in different proportions (FR; 10, 20, 30 percent) comprising of poly(lactic acid)/organomontmorillonite (PLA/OMMT) nanocomposites had been successfully prepared by Chow and Teoh [355] using a melt compounding method. The combustion tests of prepared PLA/OMMT nanocomposites had been investigated using the vertical burning test and morphological characteristics had been determined with a scanning electron microscope. Furthermore, the thermal properties of PLA/OMMT nanocomposites had been characterized by DSC and TGA. According to the UL-

94 vertical burning test results, after the application of the flame, pure PLA was found to be burned and foamed. However, the fire resistance of the PLA had significantly increased with the entry of FR into the structure. In particular, during the UL-94 vertical burning test, PLA/OMMT/FR20 and PLA/OMMT/FR30 nanocomposites had shown the outstanding flame-retardant properties. Moreover, according to the thermal analysis results, it was seen that after addition of FR, and a plasticizer, the flexibility (Tg value) of PLA/OMMT nanocomposites increased; whereas, the starting temperature of decomposition decreased. In line with these results, the research group had reported the successful synthesis of flexible and fire-resistant PLA/OMMT nanocomposites having a compact, consistent and sustained preventive sheet characteristics.

In a similar study, Cheng et al. [356] synthesized polylactic acid/aluminum trihydrate/modified montmorillonite (PLA/ATH/MMT) nanocomposites and investigated the thermal and combustion behavior. The prepared PLA/ATH/MMT nanocomposites were subjected to the evaluation of thermal stability, morphology, and mechanical properties. The flame retarding behavior was determined with a vertical burn UL94 test and cone calorimetry. According to the obtained results, MMT and ATH increased the thermal decomposition activation energy of PLA.

Wang et al. [357] prepared PLA-FR, PLA-FR-ZnAl ve PLA-FR-MgAl nanocomposites using the direct melt-compounding method. Flame retardants (FR) used in this study were ammonium polyphosphate (APP), melamine cyanurate (MC) and pentaerythritol (PER). Combustion tests of these synthesized structures had been determined with microscale combustion calorimetry (MCC) and cone calorimetry. Also, the morphological characteristics had been identified with WAXS, SEM and TEM devices. According to the combustion test results, combustible PLA was found to exhibit the flame-retardant property with these reinforcements.

Polyurethanes (PUs) are widely used in wood, leather, fibre, fabric, plastic and other areas due to their superior properties. However, polyurethane is a burning polymer. This may no longer be a problem by using flame retardant materials in different proportions. Since polyurethane has a huge commercial market, researchers make intensive research in this field. For this purpose, polyols derived from bio-renewable resources instead of petroleum-derived polyols are used in the synthesis of polyurethane. Gao et al. [358] prepared lignin-based stiff polyurethane foam nanocomposites. The study aimed to produce halogen-free, flame retardant rigid polyurethane foam nanocomposite based on the by-products of pulp and paper making industry. Lignin is a phenolic polymer that constitutes about 18-35% weight of wood and is very important as a bio-renewable source because of being quite abundant and having hydroxyl, methoxyl, carbonyl, and carboxyl functional residues and is widely used in composite structures. For the commercial applications, halogen-free flame retardant (RPUF) nanocomposite structures had been synthesized using flame retardant polyols (FRP), microencapsulated PU with ammonium polyphosphate (MAPP) and layered double hydroxide organically modified (OLDH). The thermal conductivity, mechanical, thermal stability, flame retardancy, and fire behavior properties of prepared nanocomposites had been extensively investigated. According to the combustion test results, it was found that the flame-retardant characteristics of the material were improved with the doping of FR into polyurethane foam nanocomposites.

Kord et al. [359] prepared high-density polyethylene/rice hull flour nanocomposites. Organomodified montmorillonite (OMMT) was doped into the prepared nanocomposites (Figure 49). The study aimed to regulate the effect of OMMT carrying the flame retarding property supplemented into the nanocomposites containing bio-renewable resources. According to the results of the combustion test, the author demonstrated that when the supplemented content of OMMT into the nanocomposite was increased, burning velocity, the total smoke generation and the rate of heat release from samples decreased.

Prabhakar and Jung-il studied the fabrication and characterization of S/CH/flax fabric as flame-retardant composites [360]. They revealed that flame retardancy properties were improved with the incorporation of a filler.

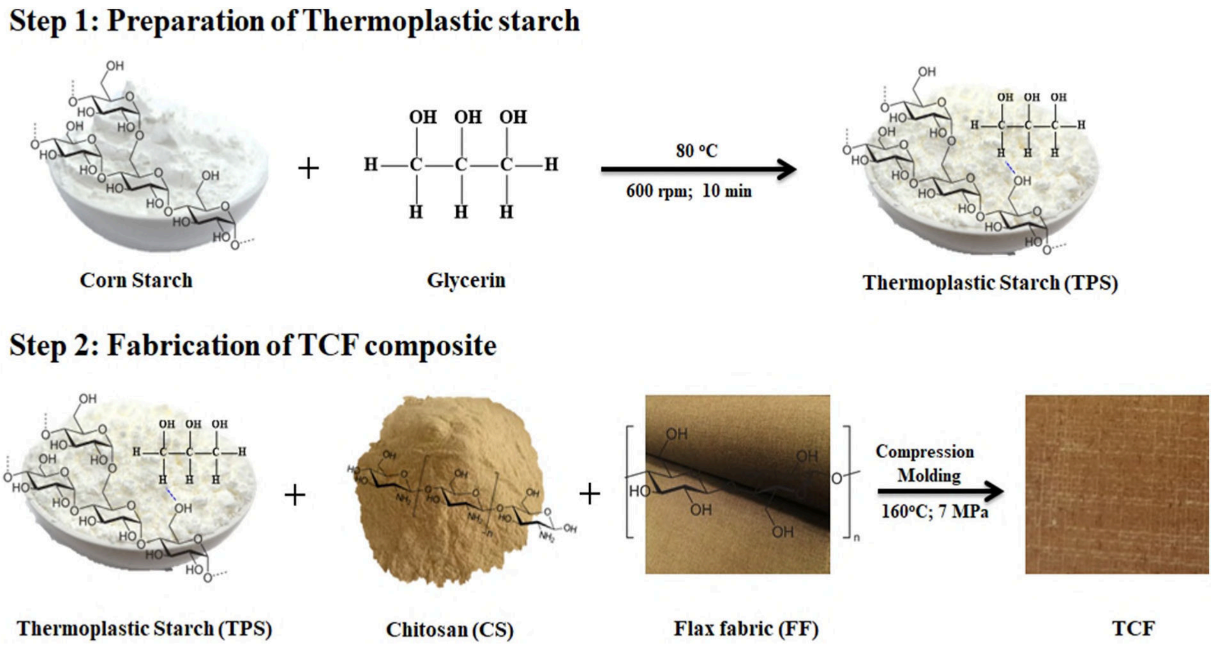


Figure 49. Schematic diagram of the procedure of TPS preparation and TCF composites fabrication. Reproduced with permission from ref [360]. Copyright 2018 Elsevier.

In another study, Wang et al. reported on the coating of lignocellulose composite with PDMS@stearic Acid-Al$(OH)_3$ as a mean to control the flame retardancy (Figure 50). The obtained results revealed that the superhydrophobic surface of the prepared composite has desirable flame retardancy. [361]

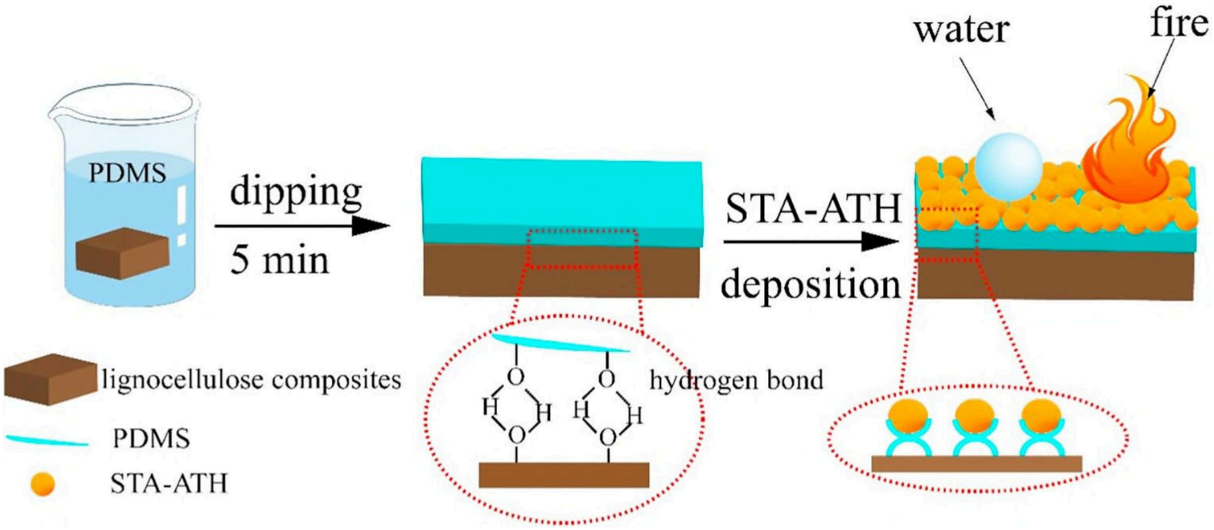


Figure 50. Schematic diagram to fabricate PDMS@STA-ATH coating on the LC surface. Reproduced with permission from ref [361]. Copyright 2018 Elsevier.

9. Other Applications

In the fields of chemistry, medical, biomaterial, electronics and optics, there is significant literature on nanocomposites obtained from bio-renewable sources. Especially, nanocomposites formed from bio-renewable resources as biocompatible materials have received increased attention in recent years. Advanced applications of nanocomposites from bio-renewable resources have come to the forefront in: catalyst [362], blood compatibility Nanodevices [363], ionotropic gelation [364], protein carriers [365], and spin-crossover property materials. [366]

For the C-H activation and electro-oxidation of ethanol, Jayarajan et al. [362] have developed amyloid fibril-palladium nanocomposite as a sustainable catalyst. Silver (Ag), copper (Cu), Palladium (Pad), platinum (Pt), and gold (Au) nanocomposites were synthesized using α-Syncline (α-Sin) fibrils as a template and characterized by using various methods such as FTIR, TEM, XPS, XRD, EDAX, and TGA. "This work revealed that α-Syn-PdNPs can be used as a promising heterogeneous catalyst for the synthesis of pharmaceutically valuable benzofuran, naphthofuran, coumarin and *N*-arylindole through C-H activation". In addition, α-Syn-PdNPs exhibited excellent electrocatalytic performance for the electro-oxidation of ethanol.

Recently, the use of heterogeneous catalysts for organic synthesis has received considerable attention. Hence, Mahdavinasab et al. [367] prepared magnetic CH/GO composite supported copper as a recyclable nanocatalyst (heterogeneous) in the synthesis of triazoles. The reaction products were attained in excellent yields within very short reaction times. Moreover, the proposed biocomposites based heterogeneous catalyst can be successfully recovered and recycled for nine runs (yield: 95%) without significant loss of activity. When the authors compared their prepared catalyst with the performance of other previously reported heterogeneous catalysts, they reported that the catalyst proposed in this study had much less reaction time, magnetically separable, stability and cheap.

In another work, Zheng et al. [368] prepared porous CH/RGO microspheres supported Pd nanoparticles catalysts for Heck coupling reactions. The catalysts were investigated via XPS, Raman spectroscopy, SEM, EDX, HR-TEM, TGA, and XRD. The prepared catalyst exhibited excellent catalytic activities for the Heck reactions between alkenes and aromatic halides. Besides, it can be reused for 13 times (yield: ~80%) without a significant decrease in coupling yields.

"In 2018, magnetic GO-ionic liquid grafted CH composites anchored Pd (0) nanoparticles were fabricated as a strong heterogeneous catalyst having enhanced activity along with superior reusability for hydrogen generation from ammonia borane" [369]. The suggested magnetic catalysts exhibited outstanding catalytic activity and greater reusability for the ammonia borane hydrolysis. Therefore, it can be used for the growth of hydrogen energy.

In 2019, Daraie and Heravi [370] developed a biocompatible CH-ionic liquid hybrid catalyst to synthesize 1,2,3-triazoles. The CH-ionic liquid hybrid catalyst was comprehensively characterized via ICP, FTIR, XRD, SEM, ^{1}H NMR, TGA, and EDX methods. The developed heterogeneous catalyst was successfully used in the reaction of terminal alkynes, sodium azide, α-haloketones or alkyl halides in water to prepare 1,4-disubstituted-1,2,3-triazoles. Additionally, the catalyst could be recycled for 5 reaction cycles with trivial CuI leaching and a slight drop in catalytic activity.

Murugesan et al. [363] had prepared carbon nanotubes based neoproteoglycans nanocomposites for potential Nanorobots having *in vivo* applications. Activated partial thromboplastin time and thromboelastographic data show that heparinization can be considerably improved depending on the nanomaterials blood compatibility. CH nanoparticles have been widely selected due to their high ionotropic gelation; calcium carbonate and clay particles are chosen because of the relatively low effectiveness of the material, and Au and Ag's nanoparticles are used because of their antibacterial properties. Especially, the biological properties of CH make it an ideal candidate to create nanoparticles for medical applications. The ionotropic gelling technique includes sodium tripolyphosphate as the most important technique for ionic crosslinking of CH with low molecular weight and hydrophobic counter ions and high molecular weight ions.[371] CH microspheres are the most widely studied systems as potential carrier matrix for drugs [372], protein [365], anticancer agents and vaccines [373]. TiO_2 and ZnO nanoparticles are often used for the self-cleaning nanocomposites obtained bio-renewable sources with renewable biopolymer matrix due to their high photocatalytic properties. In other applications, Tokarev et al. [366] synthesized nanocomposite materials having very small (3 nm) Hofmann clathrate $[Fe(pz)\{M(CN)_4\}]$ ($M = Ni^{2+}, Pt^{2+}, Pd^{2+}$) nanoparticles embedded into CH and alginate as a biopolymer. These nanocomposites have good spin-crossover (SCO) properties. Moreover, they proved the specific morphology of the matrix and the importance of 3 nm nanoparticles in the biostability.

In another study, the amyloid–metal nanoparticle hybrids displayed catalytic activity in the reduction of 4-nitrophenol into 4-aminophenol.[374] Most importantly, the amyloid–metal nanoparticle displayed enhanced catalytic efficiency in comparison to the particles without amyloid fibrils. Therefore, the catalytic ability of amyloid–metal nanoparticles can play an important role to design membranes for efficient continuous flow catalysis.

10. Conclusions and the Future Directions of the Researches on Nanocomposites from Bio-Renewable Resources

Renewability in materials preparation is an increasing new topic to maintain the sustainability of the ecosystem[375]. It is an obligation to develop new bio-renewable resource-based materials due to the predictable limit of fossil sources and the increasing environmental concerns. Besides, developing materials technology[376] is focused on developing nanocomposite materials containing a combination of improved mechanical and thermal properties, environmentally friendly, biodegradable and renewability features. Cellulose, S, gelatin, CH, guar, gum, PLA, CD, natural **fibre** and oil-based polymer are most commonly used among bio-renewable resources. Nanocomposites obtained from these resources are finding a place for biomedical applications as well as membranes, sensors, energy storage, optical, automotive and flame-retardant applications. However, new developments are needed to realize these applications more effectively and cost-effectively with nanocomposites to be formed from bio-renewable sources.

There are some disadvantages in the usage of bio-renewable based nanocomposites[377]. One of the major disadvantages is the biodegradation of products such as microplastics (plastic particles, 0.1 μm–5 mm in size) that occur during rapid biodegradation. Biomass-based polymers in the nanocomposite structure quickly break down into large quantities of microplastics when exposed to a combination of sunlight and oxygen. This type of material allows for faster disappearance than conventional plastic materials. However, microplastics produced from these systems are no different from microplastics produced from petroleum-based plastics. It also takes a long time for these microplastics fragments to completely disappear under natural environmental conditions. Therefore, concerns about the rapid biodegradation process of biodegradable products have recently emerged. The most important approach to solve this problem is to prevent the formation of microplastics by producing completely biodegradable products. We also need new approaches to improve the biodegradation process of these materials.

The second important problem is that nanocomposites obtained from bio-renewable resources cannot reach the durability of petroleum-based systems in terms of mechanical characteristics. To overcome this problem, there are different approaches. Nano processing can especially improve the mechanical properties of renewable-based nanocomposites. Besides, this is very important in terms of the improvement of the biodegradability process. Nanofillers are also very important in obtaining nanocomposites with superior properties from bio-renewable sources. Nanofillers leads not only to mechanical improvement but also thermal stability, flame retardant and gas permeability increases in nanocomposite structures. Furthermore, improving the interaction between and matrix and nanofillers with surface modification is a promising approach in the future of such materials. In particular, developments in the processing technologies in nanofillers preparation can lead to new insights, in the formation of renewable bio-nano composites. Again, the types, chemical structure and density of the charge generated on the surface are one of the most critical parameters in distributing these small particles in biopolymer matrix networks. To characterize these particles in the future, researchers and scientists need complex techniques that allow better characterization at the molecular level. The rheological measurements of these materials and the development of materials with the desired rheological properties will be very important. Furthermore, the industrial scale-up of nanocomposites is still limited. This shows that various studies are still needed for the industrial applications of nanocomposites and is one of the essential research areas of the future.

Nanofillers are very important in obtaining nanocomposites with superior properties from renewable sources. Nanofillers leads to not only mechanical improvement but also thermal stability, flame retardant and gas permeability increase in nanocomposite structures. Furthermore, improving the interaction between and matrix and nanofillers with surface modification is a promising approach in the future of such materials. In particular, developments in the processing technologies in nanofillers preparation can lead to new insights, in the formation of renewable bio-nano composites. Again, the types and density of the charge generated on the surface are one of the most critical parameters in distributing these small particles in biopolymer matrix networks. To characterize these particles in the future, researchers and scientists need complex techniques that allow better characterization at the molecular level. The rheological measurements of these materials and the development of materials with the desired rheological properties will be very important. Furthermore, the industrial scale-up of nanocomposites is still limited. This shows that various studies are still needed for the nanocomposites commercialization and is one of the imperative research areas of the future.

Biodegradable packaging devices that will be used in the packaging of foods will replace plastics in the future. Bioplastics from bio-renewable sources are an important candidate and efforts to enhance the mechanical properties of these materials will continue in the future. Here, especially nanotechnology studies will take an important place. For example, a material with superior mechanical properties, such as CH, but with a low cost, will increase the likelihood that it will be converted into such materials with future advances in nanotechnology.

In particular, a reduction in water resources makes membrane technology compulsory for people to access clean water. Therefore, in the future, nanocomposites formed from bio-renewable sources are an important area in membrane technology.

Developing technology and advances in the health sector leads to prolongation of the human life span. Especially in the tissue engineering field, studies on the production of artificial organs, bio-renewable resources make the most important resource for biomedical applications. In this area, silk-based fibroin, collagen, and elastin-containing protein-based hydrogels or polymer blends have great potential and are one of the most important fields of study in the near future.

As a result, the unique properties of bio-nano composites obtained from bio-renewable sources should be the main area to found new applications and opportunities for “green” and “nano” materials world in the next centuries. These nanocomposites with improved biocompatibility, biodegradability, thermal and mechanical properties will be used in different areas of our lives in the future.

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ABBREVIATIONS

AFM	Atomic Force Microscopy
APTES	(3-Aminopropyl) triethoxysilane
AgNPs	Silver Nanoparticles
AuNPs	Gold nanoparticles
BC	Bacterial Cellulose
BC/PANI	Bacterial cellulose/polyaniline
BCA	BC/Alginate
Bo	Boehmite
BPA	Bisphenol A
BSA	Bovine Serum Albumin
CA	Cellulose Acetate
CB	Carbon Black
CD	Cyclodextrin
CH	Chitosan
CH-MMT/PES	CH-Montmorillonite Polyether sulfone
ChOx	Cholesterol Oxidase
CM-β-CD	Carboxymethyl-β-CD
CNC	Cellulose Nanocrystals
CNF	Chitin Nanofibrils
CS–MMT	CH-montmorillonite
CSNCF	Cellulose-Silver Nanocomposites Fibre
CSnp	Chondroitin Sulfate Nanoparticles

CS-ZnO/PANI	CH-ZnO/polyaniline
EDX	Energy Dispersive X-Ray
Fe_3O_4-LNPs	Iron Oxide (Fe_3O_4) Nanoparticle Infused Lignin Nanoparticles
Fe-LNPs	Iron(III)-Complexed Lignin Nanoparticles
FE-SEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
GA	Gum Acacia
GC	Glassy Carbon
GCN-S	Graphene/Silk fibroin
GG	Gaur Gum
GO	Graphene Oxide
GT	Green Tea
HA	HA
HDPE	High Density Polyethylene
IBU	Ibuprofen
LNPs	Lignin Nanoparticles
MWCNT	Multi-Layer Carbon Nanotubes
NIR	Near Infrared
PANI/CNXLs	Polyaniline-Cellulose Nanocrystals
PBS	Poly (butylene succinate)
PDAC	Polydiallyl Dimethyl Ammonium Chloride
PEDOT/CNXL	Poly(ethylenedioxythiophene)-Cellulose Nanocrystals
PEG	Poly (ethylene glycol)

PHB	Poly hydroxyl butyrate
PLA	Poly-L-lactic acid
PLA/ATH/MMT	Polylactic acid/Aluminum Trihydrate/Modified Montmorillonite
PLA/OMMT	Poly (lactic acid)/Organomontmorillonite
PLGA	Poly (lactic-co-glycolic acid)
PLLA	PolyL-lactide
pLNPs	Pure Lignin Nanoparticles
PPG	Polypropylene Glycol
PPy/BC	Polypyrrole- bacterial cellulose
PPy/BC	Polypyrrole-Bacterial Cellulose
RCF	Recycled Cellulose **Fibre**
rGO	reduced Graphene Oxide
SDS	Sodium Dodecyl Sulfate
SEM	Scanning Electron Microscopy
SPI	Soy Protein Isolate
TEM	Transmission Electron Microscope
TEOS	Tetraethoxysilane
TGA	Thermogravimetric Analysis
THF	Tetrahydrofuran
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray diffraction

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