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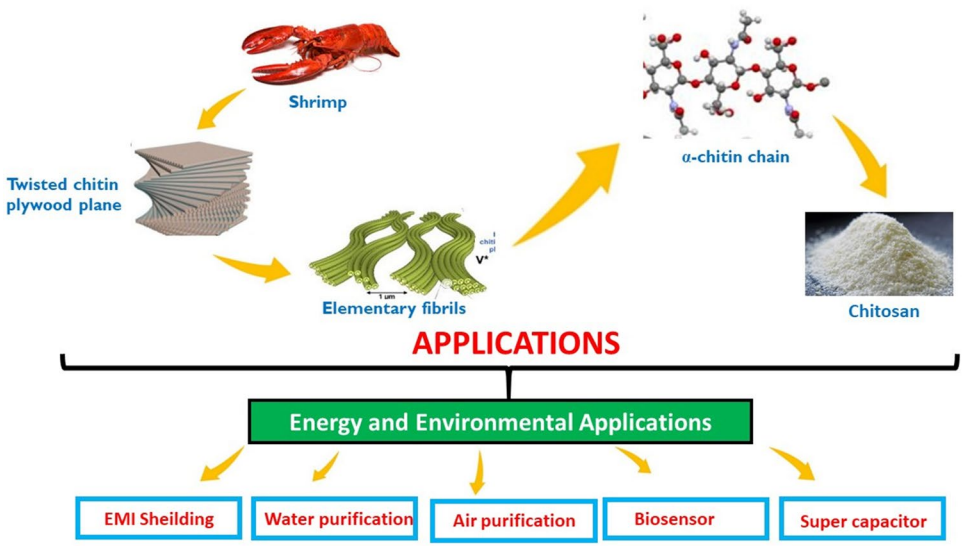
Chitin and Chitosan Based Composites for Energy and Environmental Applications: A Review

Sherin Peter[1,2] · Nathalie Lyczko[1] · Deepu Gopakumar[1,2] · Hanna J. Maria[2] · Ange Nzihou[1] · Sabu Thomas[2]

Abstract

Chitin and chitosan are the second most abundant natural biopolymers in the curst of the earth. These polysaccharide biopolymers have a long linear chain-like structure connected with β-D glucosidic linkage with the functionalizable surface groups. Because of the structural features, these biomaterials exhibit unique physical, chemical, mechanical and optical properties, which contributed to the tunable and outstanding properties such as low density, high porosity, renewability, natural biodegradability, and environmental friendliness, etc. Chitin was synthesized via mechanical, chemical, chemo-mechanical, and eco-friendly biological methods and the deacetylation of the synthesized chitin carried for the preparation of chitosan. With the chemical modification used for the preparation of chitosan, there occurs some minor change in characteristics; however, most of the properties were relatable due to major similarities in the microstructures. The inherent antibacterial, non-toxic, and biodegradable properties with the ease of processibility of both polymer has the potential to become a successful alternative to its synthetic counterparts for energy and environmental applications. However, the poor mechanical and thermal properties in comparison to the conventional alternatives have restricted its widespread applications. This review addresses various areas such as extraction techniques of chitin and synthesis of chitosan, discussion of the common characteristics of both polymers together such as crystallinity, thermal properties, mechanical properties, hydrophilicity, and surface charge. Moreover, this review paper also addresses the common functionalization techniques for both polymer and the use of both unmodified chitin and chitosan along with their derivatives in environmental and energy applications such as air pollution, heavy metal adsorption, dye adsorption, biosensors, EMI shielding, fuel cell, solar cell, lithium-ion batteries, and biofuels.

Graphic Abstract



Keywords Chitin · Chitosan · Extraction · Functionalization · Energy applications · Environmental applications

Statement of Novelty

Chitin and chitosan are polysaccharides that posses interesting inherent properties with relatively good processability. Moreover, the fascinating surface functionality of these polymers can be tailor-made for diverse as well as specific applications. These attractive properties have enticed many researchers to develop sustainable, eco-friendly, relatively easily processable, efficient products, which could replace the conventional, non-eco-friendly products in biomedical, environmental, and energy applications. Even though some reviews are reporting the biomedical applications of chitin and chitosan, there are no comprehensive reports proposed so far exclusively on their energy and environmental applications. With this contribution, we planned to fill an important gap in the literature and provide new insights into the latest trends and methods applied in this area.

Introduction

The modern industrial and technological advancements have resulted in high energy demand even for daily operations and further developments. This huge energy demand was fulfilled mostly by the exploitation of conventional and natural fossil fuels such as petroleum and its derivatives. The never-ending energy demand and uncontrolled exploitation of nature have resulted in the introduction of new pollutants to the environment, which resulted in further environmental pollution and thus forced to drive the attention of researches towards eco-friendly and sustainable resources [1]. In comparison with the conventional alternatives, the multidimensional properties of the nanocomposites such as ease of processing increased productivity, tunability, versatility and high surface to volume ration have attracted many of the researches to eco-friendly nanocomposites. The nano-size range contributed to a very high surface area which is suitable for pollutant adsorption and modification, making the nanocomposite an attractive material for energy and environmental applications. A typical nanocomposite is a multi-component material comprising of different phase domains in which at least one phase domain is a continuous phase also one of the phases has at least one dimension in the order of nanometers [2]. The continuous phase provides shape, structural integrity, maintains the relative position, and mechanical support by transferring the stress to the dispersed phase whereas the dispersed phase provides the characteristic features of the composite. The composite preparation method is significantly important for the nanocomposite since this influences the alignment of the dispersed phase in the composite system. The common nanocomposite fabrication techniques include filtration, various drying techniques, casting, electrospinning, impregnation, melt mixing, solution casting, selective dissolving etc. [3]. This led to the emergence of several research works have carried out using nanocomposite materials aiming for energy and environmental applications.

Chitin is the second most abundant natural biopolymer and the precursor of chitosan. This polysaccharide was principally extracted from the exoskeleton of certain species such as crustaceans, molluscs, insects, and even certain fungi, etc. In general, chitin is referred to as *N*-acetyl-D-glucosamine and characterized by a degree of deacetylation (DD) on the contrary, chitosan is mainly D-glucosamine characterized by a degree of acetylation (DA). The polymers exhibit certain characteristics such as antibacterial properties, non-toxicity, and biodegradability, thus it is utilized for the fabrication in a wide range of composite applications which could become the green alternative to commercially available synthetic counterparts in energy and environmental applications. The presence of multiple surface functional groups principally the hydroxyl and the acetyl or amino group results in a net cationic surface charge [4]. This surface functional group can also be manipulated to prepare a broad spectrum of derivatives with varying properties such as biodegradability, solubility in mild acidic medium, biocompatibility, degradation products are being non-toxic, non-carcinogenic and non-immunogenic. Because of these properties, it is being used in different areas such as in food and nutrition, material science, biotechnology, pharmaceuticals, agriculture, environmental protection, and energy storage [5]. Other properties like low methanol permeability, amphiphilicity, applicability in high temperature and low relative humidity environment, makes chitin and chitosan an excellent candidate for solid polymer electrolyte for polymer electrolyte-based fuel cells. Similarly, the high adsorption capacity towards contaminants, ease of physical and chemical modifications, and resistance to microbiological degradation, inherent availability of amino (NH_2) and abundant hydroxyl (OH) groups and affinity towards heavy metal makes chitin and chitosan as ideal candidates for the environmental applications [6]. The recent advancement in chitosan-based composites resulted in the evolvement of various studies which would further enhance its applicability in varying technological applications. This exploration plays a significant role in fabricating sensitive sensors, dye adsorbents and many biomedical products.

In this review, the main emphasis is given to the different functionalization techniques, properties of both the

biopolymers, application in environmental and energy areas for both the polymer in together. Even though the microstructure of both chitin and chitosan is different, it is also important to note that the difference arisen is due to different concentrations of *N*-acetyl-D-glucosamine and D-glucosamine repeating units. Both polymers are differed by the difference of these two repeating units only. Because of this particular reason, the characteristics of chitin is mentioned in the beginning all section and then compared it with chitosan for the better analysis. However, chitin is not being studied as much as chitosan, this leads to an unbalance in terms of the number of works that have carried out using both the polymer which is also reflected in this review. The review tried to provide a good balance between chitin and chitosan, however, the balance is tilted towards chitosan as a reflection of extensive works carried out in chitosan.

Chitin and Chitosan: Structure, Extraction, Properties and Functionalization Techniques

Chitin is a linear polysaccharide composed of two monomer units namely *N*-acetyl-2-amino-2-deoxy-d-glucose (*N*-acetyl-D-glucosamine) and (2-amino-2-deoxy-d-glucose) D-glucosamine units which are linked by 1–4-β-glycosidic bonds. Chitin is isolated from the exoskeleton of sea species and a typical hierarchical structure from shrimp is shown in Fig. 1 [7]. The structural difference between the chitin and chitosan depends upon the compositional difference between the two monomer units. In chitin, *N*-acetyl-2-amino-2-deoxy-d-glucose monomer was found in higher concentration, whereas the chitosan possesses a higher number of 2-amino-2-deoxy-d-glucose monomer in the main structure. Because of this, chitin is less soluble in acidic solvents whereas the chitosan obtained by deacetylation (DA) of native chitin is soluble in acidic aqueous solution due to $–NH_2$ protonation. As a rule, the polymer having 2-amino-2-deoxy-d-glucose content concentration beyond 50% considered to be chitosan and lower than 50% considered as chitin. A typical monomer has two hydroxyl groups which include one primary hydroxyl at C-6, one secondary hydroxyl at C-3 and amino groups or *N*-acetyl group (at C-2) positions [8]. The *N*-acetyl group can form linear inter and intramolecular hydrogen bonds which would be resulted in the higher crystallinity, increase in molecular weight and insolubility in water. The difference in molecular weight can be great as much as 10° Da. Chitosan is also the only commercially available water-soluble cationic polymer due to the positive charges by its amino groups. It can be differentiated from chitin by molecular mass, degree of deacetylation, crystallinity, moisture and protein content. Among all the different parameters, the degree of deacetylation is the most influencing factor which can determine the final properties of chitosan. For instance, the deacetylation can influence the solubility, flexibility, polymer conformation, surface area, porosity, conductivity, tensile strength, crystallinity, biodegradability, biocompatibility, mucoadhesion, hemostatic, analgesic, adsorption enhancing, anti-microbial and antioxidant properties [9].

Chitin is present in nature mainly in three polymorphic forms such as α, β and γ as which is schematically depicted in Fig. 2. Different forms have different properties depending upon the various microstructures. The α structure has

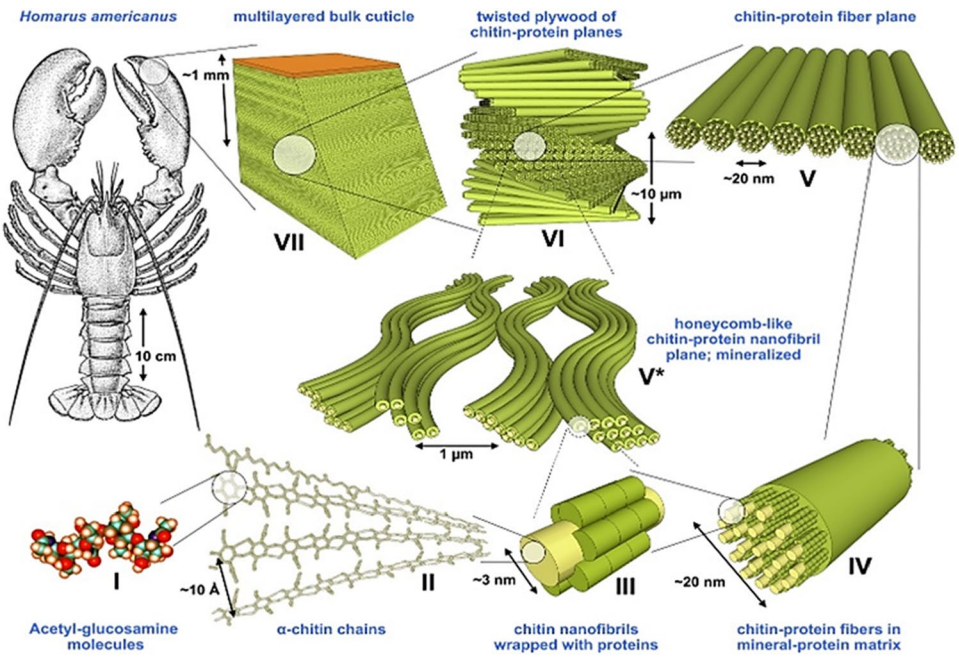


Fig. 1 Graphical illustration of the hierarchical structure of chitosan [7]

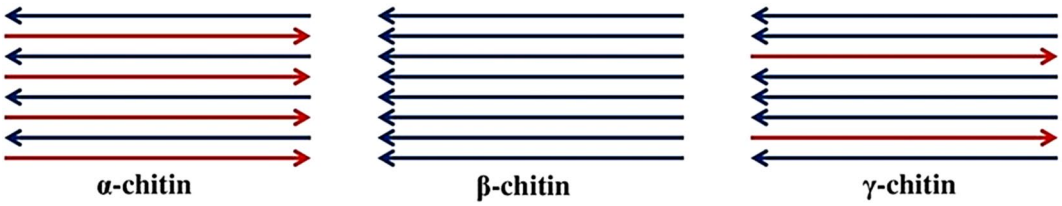


Fig. 2 Schematic representation of the three polymorphic forms of chitin [10]

the antiparallel alignment with the highest crystallinity and this is the most abundant among all the three. This is mainly obtained from the exoskeleton of crabs, lobsters and shrimp, insect cuticles, fungal, yeast cell walls and marine sponges. The β structure has a parallel alignment which is mainly obtained from squids, extracellular fibres of diatoms, spines and chaetae of certain annelids. The γ structure has a mixed alignment where two parallel chains followed by one antiparallel chain in the common source. Chitosan, on the other hand, have a noticeable heteropolysaccharide structure with linear β-1,4-linkage between the units [10]. The quantity and the order of arrangement would influence the property of the material under varying conditions. For instance, under the heterogeneous conditions, the polymer exhibits the irregular distribution of *N*-acetyl-D-glucosamine and D-glucosamine units with mainly random and a small extend of block-wise distribution. The physico-chemical properties of such chitosan found to differ from randomly acetylated chitosans obtained under homogeneous conditions.

Nanochitin Extraction

The extraction of chitin consists of two steps, demineralization and deproteinization. In the demineralization step, the calcium carbonates and calcium chlorides get removed in dilute hydrochloric acid HCl solution. During the deproteinization step, removal of protein is carried out in dilute sodium hydroxide solutions. This further washed many times with deionized water to remove excess NaOH. For the extraction of chitin, chemical and biological (microbial) methods have been employed. Other than the conventional method, microwave irradiation is being widely studied as an emerging method with high deacetylation efficiency, it is mostly preferred for the preparation of chitosan however the large degradative effect on chitin during isolation is a disadvantage. Normally, the biological methods have been used for the extraction of chitin for the laboratory purpose and this is limited by its longer processing time. The chemical method is being widely used for industrial application even with the disadvantages such as expensive processing, non-eco friendliness and partial degradation of chitin during the processing [11]. In recent times, more attention has been given to the biological methods as it is more ecofriendly. A typical composition of various chitin sources is given in Table 1.

Chemical Extraction

For the production of chitin and their derivatives from resources with simple, economical, time-saving manner, the chemical methods fulfil all the above-mentioned requirements. These chemical methods are easy to commercialize to the industry level due to the overall efficiency of the process compared with other methods. Chemical extraction consists of three steps namely deproteinization, demineralization and decolourization. The deproteinization could be carried out in the alkaline environment whereas demineralization would be carried out in the acidic environment followed by the decolourization by organic solvents [17]. In the first step, the material would be reacted with HCl to remove mineral constituents such as calcium carbonate and calcium phosphate. Stirring with 3% Sodium hypochlorite (NaClO) for 10 min was found to be more efficient for energy saving in the demineralisation. HCl, HNO_3, H_2SO_4 were some of the

Table 1 Proximate composition of different chitosan sources

Sources	% Protein	% Ash	% Chitin	% Moisture	% Lipid	References
Crabs shells	16.7	66.6	16.7	–	–	[11]
Insect cuticles	39.8	11.7	36.6	8.7	2.7	[12]
Mussel shells	10	23.3	23.5	–	–	[13]
Shrimp shells	32.8	32.5	36.4	45.7	–	[14]
Shrimp shells (*P. longirostris*)	29.3	25.1	27.0	3.6	15.5	[15]
Shrimp shells (*Penaeus durarum*)	34.0	42.3	23.7	–	–	[11]
Squid gladius (*L. vulgaris*)	36.5	2.7	31.2	–	0.3	[16]

other commonly used acids for deproteinization. After the use of strong acids for deproteinization, the demineralization of the shells was carried out using NaOH. To avoid deacetylation, partial degree of acetylation and property degradation, the deproteinisation could preferably carry out in ambient temperature with a stirred reactor which would help to reduce the duration of the process. Finally, to obtain a colourless product, acetone or an organic solvent mixture were used [18]. The chemical extraction has certain advantages like shorter processing time, a high degree of deacetylation, industrial viability and complete removal of organic salts. But the lack of environmental friendliness is a major drawback for this approach.

Biological Extraction

The biological method has gained considerable attention recently due to the drawbacks of the chemical extraction method. Chemical methods are extremely hazardous, energy-consuming which causes a threat to the environment due to the high concentrations of mineral acid and chemicals employed for extraction [19]. This has led to a growing interest in optimizing the isolation process with minimum chitin degradation, less waste production, limiting pollutions and invoke impurities to the level of invaluable application. There has been a significant improvement in this regard and high-value commercialized by-products such as chitinases, lactic acid, chitooligosaccharides, antioxidants, valuable protein hydrolyzates, carotenoids etc. have been synthesised by biological methods. There are new biological techniques developed which were found to be more efficient to isolate bioactive compounds from marine wastes at lower processing cost. Typically, lactic acid-producing bacteria are reported to be used for the demineralisation of the chitin, where lactic acid reacts with the calcium carbonate to form calcium lactate and this calcium lactate can be removed by washing. Some bacteria such as *Pseudomonas aeruginosa K-187*, *Serratia marcescens -censFS-3*, *Bacillus subtilis*, *Bacillus cereus* and *Exiguobacteriumacetylicum* were found to be capable of deproteinisation by fermentation [20]. This method has the advantages of being environmentally safe with the high quality of the final product. The minerals and proteins which have been isolated during the extraction could be used as human and animal nutrients. But the process lacks its attraction due to the prolonged processing time and limited to laboratory-scale studies.

Chitosan

Chitosan is the deacetylated form of chitin and which is composed of both *N*-acetyl-2-amino-2-deoxy-d-glucose and D-glucosamine in the chitin which is linked through β-(1−4) glycosidic linkages. However, chitosan has a degree of deacetylation beyond 50% in comparison with its precursor chitin which resulted in some characteristic changes in the behaviour. In contrast to chitin, some of the characteristics are the unique identity of chitosan such as the distribution of acetyl groups along the chains, the average DA, solubility and the molecular weight [11]. The characteristic difference between chitin and chitosan are mainly derived from the compositional difference of *N*-acetyl-2-amino-2-deoxy-d-glucose and D-glucosamine monomer units. Hence, to understand the characteristic of chitosan, determination of its average DA is of prime importance. There are many characterization techniques available for measuring the average DA in chitosan sample, Among these characterization techniques, NMR is considered to be the most convenient technique. ^{1}H NMR provides good accuracy measurement of acetyl contents in the soluble samples, ^{15}N NMR provides quantification of acetyl content from 0 to 100% in solid samples and ^{13}C was found to be optimal for measuring the entire range of DA, despite the state of the sample [21]. The preparation of chitosan from chitin plays an important role in the distribution of the acetyl group in the chitosan polymer chain. In general, the random distribution of acetyl group obtained under the homogeneous condition and blockwise distribution of acetyl group obtained under heterogeneous condition. The understanding of distribution is particularly important since it determines the inter-chain interactions and hydrophobic character due to H-bonds and acetyl groups respectively. Another important characteristic that the DA directly influence is the solubility of chitosan. This is particularly important since as per some researchers, chitosan is the deacetylated form of chitin which can be considered as chitosan only when it becomes soluble in aqueous acidic media. The solubility occurs by the formation of the inter-chain interactions derived from H-bonds and also the deacetylation results in the replacement of hydrophobic groups with hydrophilic amino groups. The better understanding of solubility mechanism has resulted in many modification studies of chitosan for improving the solubility and eliminating the same also [22]. Another important characteristic exhibited by chitosan is the dependence of the size of the polymer chain which determining its physicochemical properties. Various studies have been carried out based to understand the relationship between molecular weight and property of chitosan. It was observed that a certain number of repeating units are necessary for exhibiting high antimicrobial activity whereas another study proposed that the molecular weight increased the molecular stiffness of the polymer. Similarly, it was evident that the change in the microstructures directly reflected in the characteristics of chitin and chitosan biopolymers [23].

Preparation of Chitosan

The preparation of chitosan is usually carried out mainly by deacetylation of chitin. So, in general, the process of chitosan extraction comprises of two steps namely the extraction of chitin and deacetylation of chitin. The deacetylation is the process which removes the hydrophobic acetyl groups and replacing with reactive and hydrophilic amino groups. Generally, chemical hydrolysis and enzymatic treatment are the two most important deacetylation methods. In chemical hydrolysis, either acids or alkalis are used to deacetylate chitin for the chitosan extraction, but alkali deacetylation is used more frequently due to the higher efficiency [10]. Even though the alkali treatment is widely being employed, it also has its drawbacks such as the high energy consumption, waste of concentrated alkaline solution, environmental pollution and a broad range of soluble and insoluble products. To overcome these drawbacks and to make the process environmentally benign, the deacetylation of chitin was carried out using enzymatic method conventionally. The lower production rate is the major drawback of the enzymatic approach. Due to the major drawbacks of conventional chemical and biological methods, many researchers have studied a wide variety of techniques such as electrochemical, photochemical, sonochemical, enzymatic and microwave or radiofrequency synthesis method to find an alternative process for the chitosan extraction. Among the different methods, microwave irradiation has gained considerable attention for the extraction of chitosan due to the rapid nature of the reaction [24].

Emerging Extraction Techniques

Conventional extraction techniques had to compromise between large scale production and economical impacts. Hence, many techniques have emerged which provided the perfect balance between scalability and economical friendliness. Usage of microwave extraction instead of the conventional method could reduce the overall processing time up to 50 min with moderate substitution. The use of alkaline-based environment assisted microwave irradiation was found to be much efficient for the deacetylation of chitin. The degree of deacetylation of chitosan from different sources such as shells of fish, shrimp and crab were found to be 75%, 78%, and 70% respectively by this method. Compared to the conventional extractions, microwave synthesis could substantially reduce the reaction time, increase the yield and purity by reducing unwanted side reactions [25]. Another interesting method was to use both acidic and basic environment for chitosan isolation. This process could reduce the overall processing time to a few minutes with around 83% of deacetylation. From previous results, it is evident that microwave technology has gained a considerable amount of attention for the extraction of chitosan for the future. The authors have claimed to reduce the processing time by 1/16 times. The combination of chemicals along with the use of the microwave has provided better control over the process since they changed the power of the microwave-based on extraction stages [26].

Summary

While there are some reported extraction techniques for chitin from the bio-resources, among these different methods, chemical and biological methods are being widely employed. The conventional chemical method is dominating the industrial-scale production as it is more efficient in terms of scaling up while the operating time remaining significantly lower compare in comparison with the alternative biological approach. But, the overall applicability of this method was limited due to its non-usability in the biomedical application and being non-ecofriendly. The currently available alternative was biological methods but this approach lacks in poor scalability however the emerging technique has managed to combine the advantages of the chemical method without having its disadvantages. There was a significant increase in emerging techniques which offers versatile practices such as electrochemical, photochemical, sonochemical, enzymatic, microwave and radiofrequency techniques etc. So far microwave-based isolation method has the potential to be the key technique for the isolation of chitosan with lower production time and higher purity and efficiency. This could lead to chitosan extraction with convenience since it can bypass the extraction of chitin when combined with acidic or basic environment.

Characteristics of Chitin and Chitosan

Properties of chitin and chitosan vastly depend upon the source, deacetylation, protein content and extraction methods. Among the various parameters, deacetylation is the most significant parameter. Even though many of these are differentiating factor between chitin and chitosan, the microstructural features remain similar since the polymers contain both *N*-acetyl-D-glucosamine and D-glucosamine units. Hence, to summarize and to provide an overview of some of the most important properties exhibited by both the polymers. We have briefly mentioned below properties such as crystallinity, thermal characteristics, hydrophilicity and surface charge together. The properties of chitin are mentioned in the beginning and compared it with the properties exhibited by chitosan.

Crystallinity

The crystallinity of one of the important characteristics exhibited by polysaccharides, in the case of chitin and chitosan, the crystallinity depends upon the ratios of the different monomer present in the chitosan. The biopolymer is normally considered as chitosan when the *N*-acetyl-2-amino-2-deoxy-d-glucose (*N*-acetyl-D-glucosamine) content is more than 50. The deacetylation process employed for the extraction of the chitosan could result in the reduction of crystallinity of the chitosan and this was due to the disruption of extensive intermolecular hydrogen bonding which presents in the chitin. In general, chitin has a higher crystallinity which is brought to the low reactivity while the chitosan more reactive overall. Chitosan has been identified by the strong reflections at 2θ around 9–10° and 2θ of 20–21° and weak 2θ values at 26.4° where the XRD band at 9.9° corresponds to a d spacing of 8.92 Å and the reflection at 19.4–20° corresponds to a d spacing of about 4.4 Å respectively [27]. Anayancy et al. portrayed that, number of deacetylations was proportional to the crystallinity index of the chitosan. This was explained by the twofold helical symmetry and the conformation in the unit cells which were stabilized by strong O3 ···O5 and weak O3 ···O6 hydrogen bonds within a repeating period of 10.4 Å [28]. The influence of deacetylation process on crystallinity at various stages of extraction has been demonstrated in a study carried out by Knidri et al. (Fig. 3) where they observed that commercial chitosan, chitosan extracted by conventional heating via the chemical method and chitosan extracted by microwave heating exhibited different crystallinity index values of 51, 57 and 65% respectively. Also, the chitin exhibited the higher crystallinity index values of 90% and 78% after microwave and conventional heating respectively. This indicated the influence of the method of extraction on the crystallinity values of chitosan obtained [26].

Thermal Properties

The degradation of chitin or chitosan occurs via the cleavage of glycosidic linkages. This can be observed in the study carried out by Paulino et al. where they observed the two-step decomposition for chitin and three-step decompositions for chitosan respectively as depicted in Fig. 4. In the case of chitin, the first step of thermal decomposition occurs in the temperature range of 50–110 °C, which is attributed to the water evaporation. The second step of thermal decomposition occurs in the range of 300–400 °C which attributed to the degradation and dehydration of saccharide rings, decomposition of acetylated, and deacetylated units. However, after heating at 1000 °C the percentage of residual mass was around 36% and could suggest the presence of minerals that were not extracted in the acidic stage [4]. Similarly, in the case of chitosan, the first step of decomposition was due to dehydration and this has the peak value at 168 °C. The main thermal degradation has appeared between 230 and 400 °C with a maximum peak of 273 °C. This could be attributed to the depolymerization of chitosan chains during which the polymer experiences a 43% of mass loss. This was mainly attributed to multiple reasons such as decomposition of pyranose rings by the dehydration, ring-opening reaction, and de-amination [29]. The chitosan undergoes a strong thermal oxidation reaction after 400 °C and reaches a maximum of around 430 °C. The main peak at 430 was due to the oxidation reaction which resulted in the further decomposition of oxidized chitosan which led to the chain scission with the formation of volatile degradation products. Similar to crystallinity, the thermal properties of chitosan are also different from chitin. The higher stability of the chitin

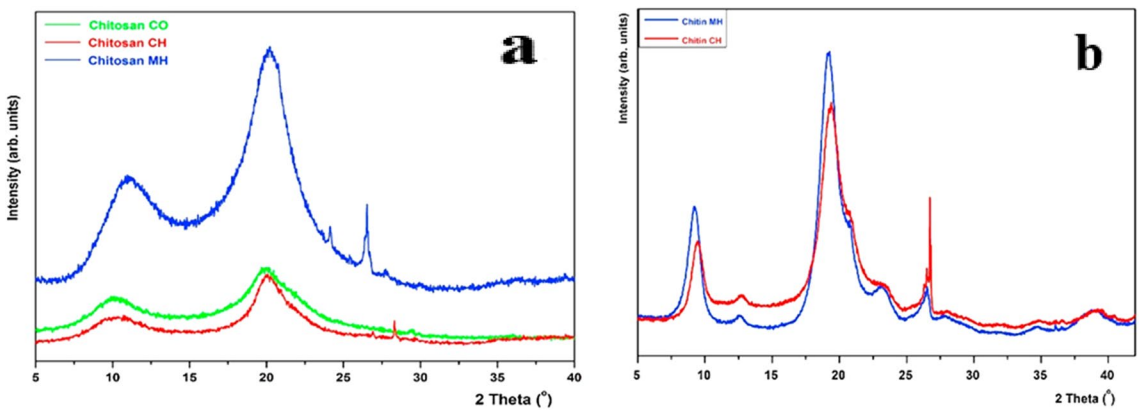


Fig. 3 XRD patterns of **a** chitosan CO (commercial chitosan-green), chitosan CH (chitosan prepared by conventional heating via the chemical method—red colour), chitosan CM microwave heating chitosan prepared by microwave heating (blue colour) **b** chitin extracted by chemical heating (red colour) and microwave heating method (blue colour) [26]. (Color figure online)

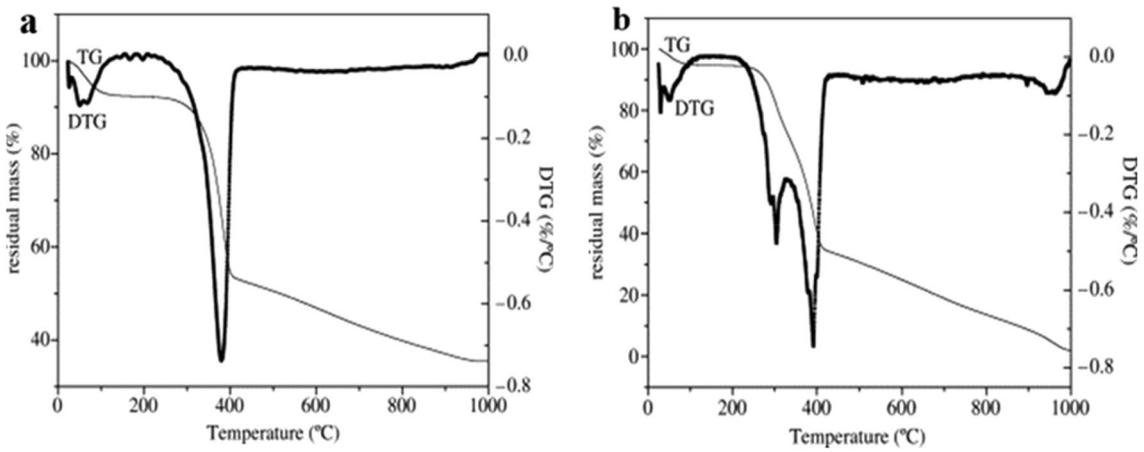


Fig. 4 TGA of **a** chitin extracted from silkworm chrysalides **b** chitosan produced from silkworm chitin [4]

could be explained by the extensive intermolecular hydrogen bonding [30].

Hydrophilicity

Contact angle measurements are carried out for gauging the surface affinity towards water. In general, 90° is considered as the critical value, where any value above this, the material is considered as hydrophobic and below which, the material is considered as hydrophilic. Kaya et al. studied the surface affinity of chitin towards the water for both natural and synthetic originated materials. They have observed contact angle values of $68 \pm 2.51°$ and $19.7 \pm 1.9°$ for both natural and synthetic originated chitins respectively. This drastic difference has been explained by preparation used in the synthetic chitin where it contains glycerol which was incorporated as a plasticizer. The glycerol has high water binding capacity which was observed in some other studies [31]. In contrast, chitosan having two hydroxyls and one amino functional group per repeating unit resulted in an amphiphilic nature. This presence of the surface functional groups has made chitosan a pH-sensitive material. Also the as a function of the protonation intensity of the amino groups in the acidic medium, this resulted in a more hydrophilic nature at low pH values whereas exhibiting hydrophobicity at higher pH values. This amphiphilic nature was reported in contact angle studies because the final state of a water drop on the film surface is taken as an indication of surface wettability by water. It is well known that the water contact angle decreases when surface hydrophilicity is higher. This was also demonstrated by Britto et al. where they studied the contact angle of chitosan film in different pH values and they observed that the chitosan film in neutral pH had a contact angle of $102 \pm 2°$ but the contact angle was reduced to $89 \pm 1°$ at a pH of 3.9. Moreover, they also proved that polyelectrolyte with positive charges had more affinity towards water, this showed higher hydrophilicity than neat chitosan [32]. This could be useful in developing hydrophobic derivatives for favourable gene transfection, enhance cell binding, confer protection from enzymatic degradation and many more while the hydrophilic modification could be useful in improved intracellular pDNA release, increased water solubility.

Surface Charge

Chitin and chitosan exhibit similar surface charges even though the net surface functional groups are different. Chitin having only two hydroxyl surface groups whereas chitosan having two hydroxyl groups and amino surface groups. There is a characteristic difference between chitin and chitosan, chitin only exhibits a positive surface charge owing to the acidic hydrolysis employed for the isolation process. These characteristics of chitin were studied by Liu et al. where they studied surface charge of chitin whiskers in both acidic and basic condition for understanding the rheological and liquid crystalline properties. They have observed zeta potential values of + 23.9 mV and + 11.4 mV for chitin nanowhiskers which stirred in HCl for 10 min, later centrifuged to neutrality and chitin nanowhiskers which stirred in NaOH for 10 min, later centrifuged to neutrality, respectively. From the difference in zeta potential, they have proposed that protonation plays an important role in surface charge which also depends on the environmental pH. In this case, the chitin whiskers tend to lose protons in an alkaline environment which resulted in lower zeta potential values [5]. Whereas, chitosan has both positive and negative zeta potential value due to the presence of hydroxyl and amine groups which is also dependent on the pH. Chang et al. demonstrated the correlation between surface charges and the pH. The positive charge was arisen due to protonation intensity of $-NH^{3+}$ at acidic medium whereas at alkaline

medium $–NH^{3+}$ deprotonate resulting in H-bonding. The molecular weight also influences on the surface charge of chitosan as it becomes more polycationic at acidic medium since higher MW also contributed to a greater number of available $–NH^{3+}$. This also resulted in the reverse order where at alkaline medium the higher MW contributed to a greater number of hydrogen bonding due to the higher number of hydroxyl groups. This is also significant since the amount of positively charged $–NH^{3+}$ residues has a critical effect on the bactericidal activity of chitosans. The influence of zeta potentials with antibacterial activities of chitosans is shown in Fig. 5 [33]. Many studies related to the antibacterial activity of chitin and chitosan found out that antibacterial ability has a direct correlation with the zeta potential value. Du et al. demonstrated the relationship between zeta potential and anti-bacterial property by loading various metal ions into the chitosan. They concluded that the antibacterial activity was significantly enhanced which was directly proportional to zeta potential value increment [34].

Summary

Chitin and chitosan exhibit a wide range of characteristics driven from the surface functional groups and extraction mechanism used. The processability of the polymeric material makes it a relevant material in a broader application sector. The chitin exhibits very high thermal and crystallinity due to the strong intermolecular interaction in comparison with chitosan exhibits relatively weaker crystallinity index such as 64.9% and which further varies based on the extraction techniques used. Unlike the predecessor chitin, chitosan has weaker thermal stability it undergoes a two-step thermal decomposition where the 1st peak could be at 273 °C attributing to the depolymerisation of chitosan chain and strong thermal decomposition after 400 °C attributed to chain scission with the formation of volatile degradation products. The hydroxyl and the amino group influence the surface-related characteristics of the material such as hydrophilicity where chitosan exhibiting hydrophilic nature at low pH values and hydrophobicity at higher pH values. Also, the different charged surface functional groups resulted in both positive and negative zeta potential value which depends on the pH.

Surface Modification of Chitin and Chitosan

Chitin and chitosan are interesting bioactive polymers having a primary hydroxyl, secondary hydroxyl (–OH) and amino ($–NH_2$) or acetyl functional groups which could facilitate the possibilities of diverse chemical modifications. The chemical modification results in various types of derivatives with modified properties for specific applications such as pharmaceutical, biomedical, biotechnological, cosmetic, agricultural, food and non-food industries, water treatment, paper, and textile industry, etc. The ability of chitosan to undergo a wide range of surface modifications suggests its huge potential to the scientific community and industry in the current scenario. A schematic representation of chitosan-based surface modification has been demonstrated in Fig. 6 since both chitin and chitosan have similar surface modification patterns in general. Even though both chitin and chitosan modified for wide applications, in comparison to chitin, chitosan has been studied much extensively.

TEMPO Oxidation

The versatile chemical, physical and mechanical properties which can be introduced by modifying with TEMPO (2,2,6,6-tetramethylpiperidin-1-yl)oxyl have managed to attract the attention towards sophisticated applications in many fields ranging from biomedicine, energy and environmental remediation etc. There have been many studies which carried out in this regards aided for applying as

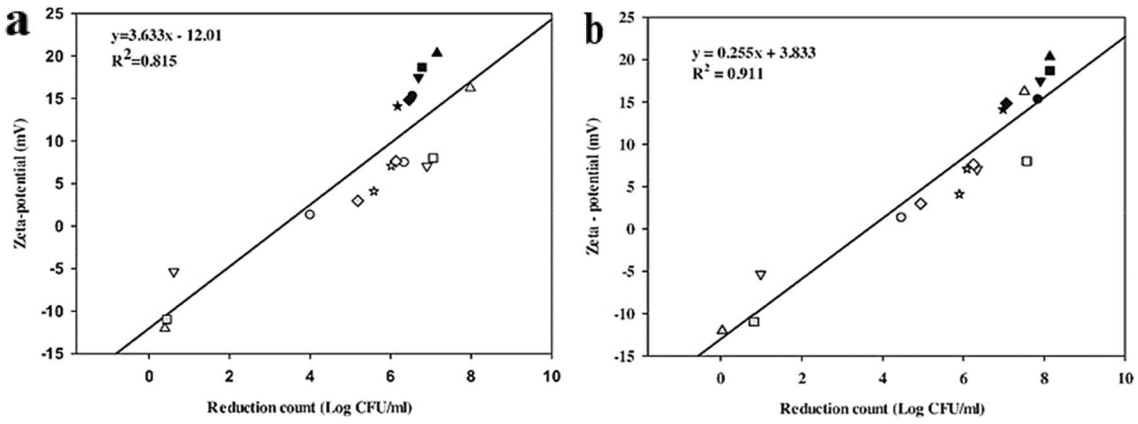


Fig. 5 Correlations between the zeta potentials and antibacterial activities of chitosans against *E. coli* BCRC 10675 (**a**) and *S. aureus* BCRC 10780 (**b**) at 37 °C for 24 h [33]

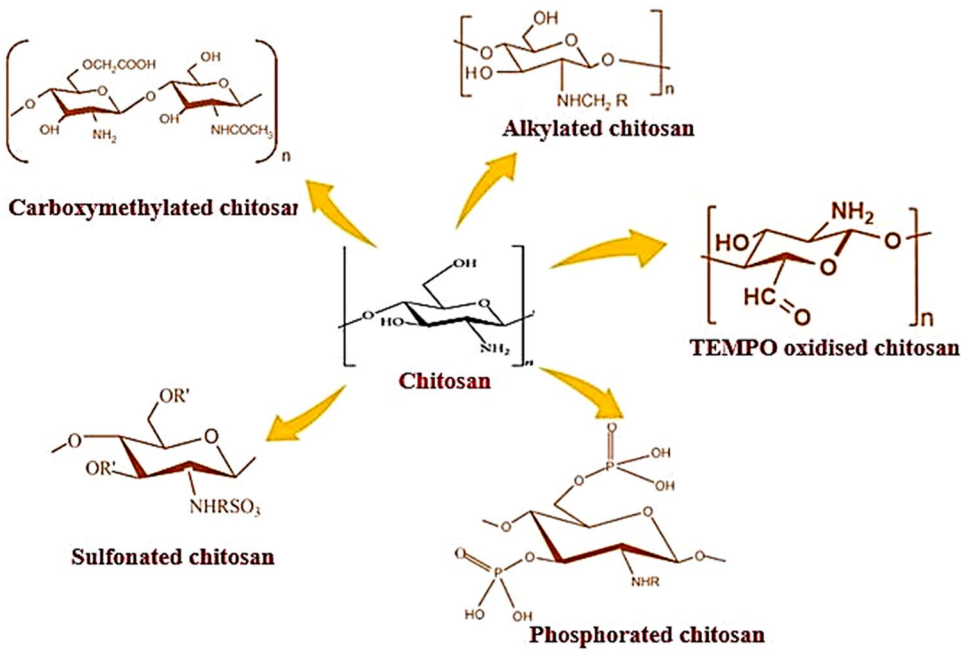


Fig. 6 Surface modification of chitosan by chemical methods

additives for specific formulations, aerogels, hydrogels etc. for advanced applications, without the need for an addition of cross-linkers. Several scientific pieces of research have explored the possibility of modifying water-soluble chitin and chitosan derivative with the use of TEMPO, which is an organic catalyst used for the oxidation of hydroxyl groups into aldehyde in NaOCl and NaBr conditions. Kato et al. explored this TEMPO modification for regioselectively oxidizing primary hydroxyl groups in both chitin and chitosan. The regenerated chitin and chitosan with deacetylation more than 93% found to be water-soluble within 70 min by the TEMPO-mediated oxidation. However, they also observed that high crystallinity of chitin and higher C2-amino group content of chitosan with lower than 77% deacetylation is unsoluble even with the modifications [35]. Sun et al. carried out TEMPO-mediated oxidation for chitin to analyse the adsorption of Cd(II) in comparison with original chitin. They have observed that the modified chitin exhibit a maximum adsorption capacity about 207.9 mg g^{-1} at 298 K by electrostatic interaction when calculated by Langmuir model [36]. Silva et al. selectively modify chitosan to fabricate a tailored cross-linked hydrogel derivative which is suitable for pH-response. The modification has introduced carboxyl and aldehyde groups into the polymer. The formed hydrogels were transparent and showed good pH-responsiveness. This opens numerous application in biomedical, environmental and other energy-related areas due to the addition of solubility and versatility to the inherent biological properties of chitin and chitosan [37].

Carboxymethylation

Carboxymethylation is one of the most commonly employed functionalization techniques which can introduce amphoteric and water-solubility. This nature of the carboxymethyl chitin and chitosan have helped in many areas such as bioimaging, food technology, theranostics, biosensors and wound healing etc. Accordingly, the more substituted carboxymethylated samples exhibited a wider range of solubility due to reduced surface charges compared to the neat polymer. This functionalization is very useful in targeted drug delivery, other environmental and engineering applications. Ding et al. synthesized carboxymethyl chitin via one-pot reaction capable of tunable protein release using NaOH/urea solution, sodium chloroacetate reacted at 15 °C for 72 h. The pH was adjusted to 7 using HCl aqueous solution, and dialyzed to neutrality over 7 days and finally freeze-dried. They further deposited this on the stainless steel electrode surface via an electrochemical method which could electrically release the entrapped bovine serum albumin (BSA) in Na_2SO_4 solution when different voltages applied [22]. Similar to chitin, the most common carboxymethyl modified chitosan is prepared by reacting with chloroacetic acid under alkaline conditions. There are principally three different carboxymethyl chitosans are formed: *N*-carboxymethyl,*O*-carboxymethyl and *N*,*O*-carboxymethyl chitosans. When the amino groups in the chitosan react with the carboxymethyl groups forms the *N*-carboxymethyl chitosan. The hydroxyl groups in the chitosan react with the carboxymethyl groups forms the *O*-carboxymethyl chitosan. However, in some cases, both the

hydroxyl and the amino group are carboxymethylated which results in the formation of *N*,*O*-carboxymethyl chitosan [6]. Borsagali et al. synthesised and employed carboxymethyl modified chitosan for the adsorption of heavy metals from industrial wastewater. They have reported having good adsorption capacities towards heavy metals with adsorption being pH-dependent. Along with the inherent hydrophilicity, biodegradability, eco-friendly nature, metal-chelating ability and nontoxicity etc. makes it a promising adsorbent for heavy metals. However, the applicability has limited by its poor chemical stability [38].

Alkylation

Similar to the carboxymethylation and TEMPO modification, alkylation is a similar modification used for chitin and chitosan because even with the extraordinary abundance in nature these biopolymer remains underutilized biomass mainly because of the poor solubility in solvents. To overcome this major disadvantage, many studies have been carried such as Kurita et al. where they fabricated alkylated chitin biopolymer by a two-step process. In the first step, they fully deacetylated the chitin using different aldehydes such as formaldehyde, acetaldehyde, and pentanal. Later these *N*-alkyl chitosans were converted into the corresponding *N*-alkyl-chitins by acetylation using acetic anhydride. This was then followed by a transesterification process which removed the partly formed *O*-acetyl groups resulting in the formation of *N*-methyl-, ethyl-, and pentyl-chitins. They have observed the modification have resulted in the destruction of crystallinity in the chitin structure. This also improved in the affinity for solvents which could also indicate the possibility in the formation of superior tractable chitin analogues. They have open the possibilities of this modification for future applications in wide areas [39]. However, in the case of chitosan, Liu et al. took a different approach for synthesising modified chitosan by alkylation at different degree of alkylation (AD). They have observed that in general, 2–4% of alkylation is preferred over higher AD value since it could lead to the formation of hydrophobic pools suitable to solubilize hydrophobic drugs. This speciality has employed in drug delivery applications of the hydrophilic and hydrophobic drugs. This alkylation modification could be employed in tuning the chitosan for a wider application range [40]. Ortona et al. tried to understand the quantitative insight about the self-aggregation behaviour of these grafted polymers in solution and physicochemical behaviour of different length at 10% AD with aliphatic chains. They demonstrated that grafting of a short chain of five carbon atoms made the chitosan structure more rigid and improved the polymer–solvent interaction rather than promoting intra-aggregation of the polymer molecules. When carboxylic anhydrides used, it was observed that the carboxylic anhydrides of chitosan having low regularity were acquired which was also water-insoluble with decreased biodegradability. Similarly, the substitution with minimum 6 or more alkyl chains showed hydrophobic characteristics [34].

Sulfation

Sulfation is an important chemical functionalization useful for a wide range of application sectors which introduce a negative charge to the surface of chitin and chitosan biopolymers along with the existing positive charge inside the polysaccharides which led to the better anticoagulation and haemagglutination inhibition activities in biomedical applications. This functionalization is mainly carried out by reacting with sulphur containing oxides like sulfur trioxide/sulfur dioxide, sulfuric acid, etc. Zou et al. prepared sulfated chitins by reacting neat chitin with sulfur trioxide pyridine complex under homogeneous conditions in LiCl/DMAc solvent mixture. They observed that the degree of sulfonation (DS) was between 0.5 and 1.9 under mild and homogeneous condition however this value increased at elevated temperature. They also observed that at room temperature, the sulfonation was mainly mono substitution resulting in the formation of 6-*O*-sulfated chitins whereas, in the case of elevated temperatures, the modification resulted in the formation of 3,6-*O*-disulfate-chitins. They also studied the influence of modification concerning the anticoagulant activity and observed no anticoagulant activity for 3-O- and *N*-sulfated-chitosan while the fully sulfated and 3,6-*O*-sulfated-chitin exhibited 45% and twofold anticoagulation activity respectively. In general, a higher degree of sulfonation tends to result better the anticoagulant activity [41]. In the case of chitosan, when chitosan is sulfated, different structural varieties of products were obtained, which is related to the different reactivities of the three functional groups in the parent polymer, leading to different degrees of completion in the individual groups. In general, among different modifications, the disulfonated derivatives exhibit better metal chelation when compared with mono-sulfonated derivatives. The disulfonated chitosan has SO^{3-} group in the para position, which has better accessibility towards the metal cations in the solution. This hinders the intramolecular interactions exhibited by the inherent positively charged amino groups [42]. Huang et al. also fabricated sulfonated chitosan by a nucleophilic substitution reaction. On comparison with the unmodified chitosan hydrochloride, the modified chitosan exhibited significantly lower metabolic and secretion activity of *E. coli and S. aureus.* The authors propose proper exploitation and understanding of this modification for the preparation of chemical preservatives in food and medicine field [43].

Phosphation

Phosphation of biopolymers has had significant importance in biomedical and anti-inflammatory properties. This has led to many scientific research studies of both chitin and chitosan in biomedical application. Khanal et al. investigated the applicability of phosphated chitin to replace the use of chitosan suspension due to acute respiratory distress syndrome caused by its overdose. During the study, they have observed phosphated chitin have significantly reduced lung injury and prevented the accumulation of neutrophils in the alveolar spaces of the lungs which were a major concern in the case of chitosan suspension. The authors also proposed that the anionic surface charge and heparinoid like activity could have aided the phosphated chitin to behave like a natural surfactant which thereby reducing the inflammation in the lungs. This modification also prevents pneumonia in the lungs. With these impressive results, the authors proposed the use of phosphated chitin as a new anti-inflammatory agent [44]. However, in the case of chitosan, the phosphation is carried out in two types, which forms two different phosphorated chitosans such as N-mono- and di-phosphonic methylene chitosan. This is synthesised by the reaction between neat chitosan and phosphorous acid or phosphorylating agent such as diethyl chloro-phosphite. The degree of substitution can be controlled by the ratio of the reagent and the chitosan. This derivative possessed insecticide properties with lower toxicity than commercial organo-phosphorous biocides [45]. Kahu et al. prepared modified chitosan with improved adsorption capacity towards hexavalent chromium from industrial effluents and other wastewater sources. The modification has resulted in the formation of multiple reactive sites which contribute towards ion pair as well as electrostatic interactions aiding in the improved adsorption of chromium ions. The authors claimed to have achieved a total chromium recovery of 94% and a maximum adsorption capacity of 266.7 mg g^{-1} following Langmuir isotherm model. Additionally, the phosphated chitosan only had a marginal reduction in adsorption efficiency after ten adsorption–desorption cycles [46]. Shanmugam et al. prepared phosphate chitosan from the cuttlebone of *Sepia kobiensis* by modification using orthophosphoric acid. They have carried out a detailed study concerning the antibacterial activity of neat and phosphated chitosan against various clinically isolated human pathogens. Interestingly, they have observed a broader antimicrobial activity spectrum for the unmodified chitosan which further strengthen the inherent property of the material [47].

Crosslinking

The undesired solubility of chitin and chitosan in the acidic condition is considered to be a major drawback. Due to which, the applicability of these materials is limited certain extend despite the excellent inherent properties. There are several functionalization techniques employed for overcoming these disadvantages. However, the cross-linking of these biopolymer using a bifunctional or polyfunctional reagents is considered to be the most efficient solution to this problem. The commonly employed cross-linking reagents include epichlorohydrin, glutaraldehyde and ethylene glycol diglycidyl ether etc. The cross-linking have the advantage of using it for water purification [48]. Chen et al. used quinone as a crosslinking agent which not only limited the solubility but also improved the mechanical strength of chitin nanofibers. They have used the quinone hardening reactions at neutral aqueous phase for the fabrication of mechanically strong hydrogel. The reaction between the surface amino groups in the chitosan fibres and the quinone molecule is expected to be the reason behind the mechanical property improvement. Since this method of crosslinking have ensured good mechanical property and keeping most of the functional groups unreacted, the authors proposed the true potential of this system in biomedical applications, especially in the biomedical engineering fields [49]. Chen et al. employed glutaraldehyde and epichlorohydrin for crosslinking chitosan in different studies and they have reported that epichlorohydrin is more efficient than glutaraldehyde due to the difference in mechanism of crosslinking. Epichlorohydrin reacts mainly with the available surface hydroxyl groups leaving the reactive amino group available for adsorption of dyes whereas glutaraldehyde reacts with the less available amino groups which reducing the availability of reactive amino group thereby reducing the adsorption capabilities [50]. Similarly, the amino group, thus decreasing the number of active sites and resulting in a decrease in the adsorption capacity. Zhou et al. studied the crosslinking effect of glutaraldehyde under homogeneous and heterogeneous conditions. The homogeneous cross-linking of glutaraldehyde resulted in increased hydrophilicity of chitosan beads due to the destruction of surface amino groups whereas the heterogeneous cross-linking of glutaraldehyde resulted in the reduction of adsorption capacity and reduction in polymer chain flexibility [51].

Graft Copolymerization

Among the several modification techniques employed for introducing various desirable properties into chitin and chitosan-based materials, graft copolymerization found to have significant importance. The ability to provide a wide range of desirable properties with great tunability which has attracted many research works in this area. There are several deciding factors which influences the efficiency of grafting such as reaction time, reaction temperature, monomer-polymer ratio, initiator concentration etc. Similarly, the molecular structure, nature of chain length and side-chain etc. play

a major role in deciding the properties of the grafted copolymer. There are many techniques of graft polymerisation for these biopolymers which has gained much attraction since its both selective, eco-friendly approach along with eliminates the use of chemical reagents and radiations. Among many of the graft polymerization [52]. Ifukua et al. prepared a graft copolymerized chitin nanofibers with acrylic acid (AA) in an aqueous medium using the potassium persulfate as a free radical initiator. They managed to prepare a better dispersion of chitin nanofiber in water with increased AA concentration. When analyzed with XRD, they observed that the grafting has occurred on the amorphous phase of chitin biopolymer. Even though the chitin-acrylic acid polymer has not fully dissolved in water, this resulted in retaining of crystalline structure which exhibited the characteristic of chitin. The main advantage with this type of grafting is the possibility of surface graft polymerization which could be applied to other vinyl monomers [53]. In the case of chitosan, Kyzas et al. successfully synthesized acrylamide-grafted chitosan microspheres for the removal of basic blue 3G dyes from water. They have employed a radical initiated graft copolymerization technique for introducing the acrylamide group into the chitosan microspheres [54]. Similar to this, Al-karawi et al. also successfully synthesized acrylamide-grafted chitosan using graft copolymerization using potassium persulfate (PPS) under a controlled environment. The acrylamide-grafted chitosan exhibited Cu(II) ion removal efficiency in proportion with the percentage of grafting. The modification found to be very effective in sequestration of Cu(II) ions in wastewater [55].

Summary

The functionalization of polysaccharides like chitin and chitosan is of great interest for many years, since it is a convenient way to improve and introduce properties and helps to prepare new materials with specialized characteristics for developing more advanced and innovative materials. In this review, we summarize the latest and most commonly applied methods for the modifications of chitin and chitosan which allow the control over the macromolecular architecture. Since the understanding of the chemical structure and properties is an important condition for proposing innovative materials. The most commonly employed functionalization includes carboxymethylation, alkylation, sulfonation, succinylation, and phosphorylation, crosslinking and graft polymerization have discussed. Even though many techniques have been adopted, carboxymethylation and alkylation found to gain more attention as the carboxymethylation is suitable for a wide range of applications since it offers relatively easier chemical modification whereas alkylation helps to develop both hydrophilic and hydrophobic derivatives.

Environmental Applications of Chitin and Chitosan-Based Composites

Chitin and chitosan-based adsorbents have received a lot of attention for application in the environmental field due to its inherent fascinating properties. Various modifications of these biopolymers in combination with other material have been investigated to improve the application in the environmental field. The mechanical and physical characteristics of these biopolymers along with its low source cost, eco-friendliness, hydrophilicity, and net canonicity make it a versatile material for the application in environmental fields. Even though, both chitin and chitosan were researched extensively for environmental application, the slight superior ease of functional ability, modification friendliness, and presence of surface amino group has resulted in many research work being carried out on chitosan biopolymer. This can be also observed in some areas where the only chitosan is being used.

Air Purification

The chitosan nanofibers with high surface area, high aspect ratio, good mechanical properties, and the ability to incorporate multifunctional nanoparticles make chitosan fibres as an effective substrate for the air filtration. In this context, a lot of literature has been reported on the usage of chitosan and its derivates for air filtration. Wang et al. developed antibacterial chitosan (CS)/polyvinyl alcohol (PVA) blend system via eco-friendly non-solvent induced phase separation (NIPS) method for air filtration application. The fabricated membrane at 30 wt% chitosan concentration and thickness of 37 μm exhibited a gradient interconnected porous structure without skin layer which had an air filtration efficiency of 95.59%. It consisted of pores of different sizes where the largest pore had a diameter of 467 nm and a surface porosity of 21.5%. The thickness of the membrane was considered to be the key parameter in the filtration performance and the direct interception on the membrane surface was the dominant mechanism for removing NaCl aerosol particles, which is schematically depicted in Fig. 7 [56]. Desai et al. fabricated nanofibrous filter media by electrospinning of chitosan/PEO blend solutions onto a spun-bonded non-woven polypropylene substrate which had different fibre diameter and filter basis weight. The filtration efficiency of the fabricated composite was strongly related to the size of the fibres and the amount of chitosan on the surface. The developed filter media using an environmentally benign, naturally occurring biodegradable biopolymer chitosan offers a lot of unique advantages and could be used as an excellent candidate for filtration purposes [57]. Zhang et al. developed an in-situ electrospun nanostructures into a polluted enclosed space to efficiently clean the air. The fabricated composite

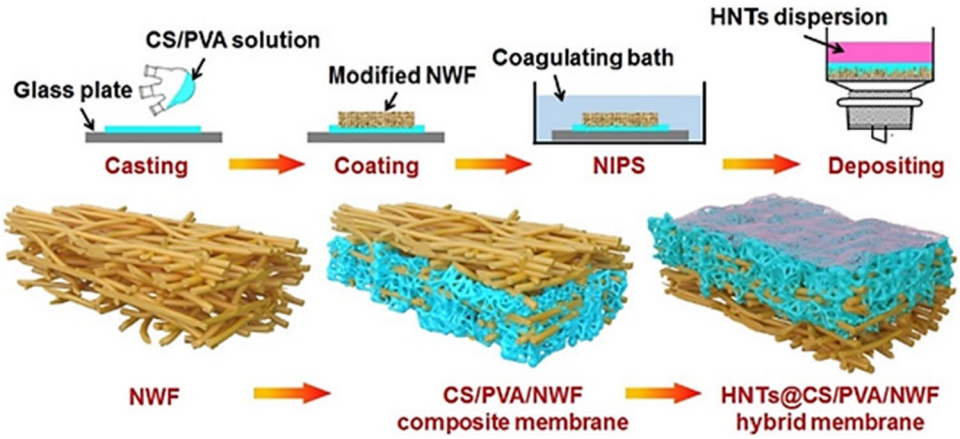


Fig. 7 Schematic depiction for the fabrication process of the HNTs@CS/PVA/NWF hybrid membranes [56]

exhibited a high removal rate of 3.7 μg m^{-3} s^{-1} with a filtration efficiency of 95% and adsorption of PM2.5. Based on higher polarity, the chitosan used in this in-situ electrospinning method had higher removal efficiency of PM2.5 than PAN, PVP, and PS, which could benefit the sufficient polarization charges on the surface of nanofibers [58]. Summary of recent works carried by chitosan for air purification application is illustrated in Table 2.

Heavy Metals Adsorption

Various adsorbents have been used to remove different types of heavy metal from various sources. Biopolymer composites based on chitin and chitosan employed widely for removal of toxic heavy metals from water. Some of the important studies show promising results. Sun et al. prepared TEMPO surface-modified chitin (SMC) which had adsorption capacity for Cd(II) with high pH dependency and the SMC reached equilibrium within 120 min. The particular modification exhibited maximum adsorption of 207.9 mg g^{-1} at 298 K when calculated by the Langmuir model [36]. Ren et al. prepared a highly efficient adsorbent which has very high removal efficiency towards heavy metals. The composite was prepared using DTA-modified chitosan with SiO_2/Fe_3O_4 and then crosslinked using water-soluble carbodiimide as the cross-linker in buffer solution. This powder was then dried out using a vacuum oven at 50 °C for 12 h in an air oven. The composite very good adsorption at low pH and exhibited much higher removal efficiency for the metal ions in comparison with a neat chitosan sample. In comparison with the neat chitosan, the modified sample have adsorption capacity in many folds. The maximum adsorption capacities of neat samples were 0.495, 0.045, 0.040 mmol g^{-1} and 0.699, 0.596, 0.563 mmol g^{-1} for Cu(II), Pb(II), and Cd(II) ions for neat chitosan and modified chitosan samples respectively. This composite had retained an adsorption capacity of 75% against heavy metals even after 12 times usage. The preparation and the influence of pH on the heavy metal adsorption are demonstrated in Fig. 8 [62]. Similarly, Li et al. developed a chitosan/sulfydryl functionalized graphene oxide composite via covalent modification and electrostatic self-assembly which resulted in the formation of multifunctional material with various functional groups such as –OH, –COOH, –SH and $–NH_2$ on the composite surface. The chitosan/sulfydryl-functionalized graphene oxide composite (CS/GO-SH) was used as

Table 2 Chitosan-based composited for air purification application

Composite	Pollutants	Method	Inferences	References
Chitosan/activated carbon/TiO_2	Toluene	Dip coating	Adsorption efficiency of 93%	[59]
Zero-valent nano-silver/TiO_2–chitosan	Bacteria and fungi	Photochemical deposition	Adsorption efficiency of 88% and 97% for bacteria and fungi within 30 min	[60]
Nanoporous PLA/chitosan nanoparticle	PM2.5, *Escherichia coli* and *Staphylococcus aureus*	Electrospinning	Filtration efficiency of 98.99% Antibacterial activity of 99.4% and 99.5% against *Escherichia coli* and *Staphylococcus aureus*	[2]
TiO_2/Ag/Chitosan	Bacteria	Electrospinning	PM2.5 concentration to decrease from 999 to 0 μg m^{-3} Antibacterial activity of 97% and 99% for *E. coli* of *S. aureus*	[61]

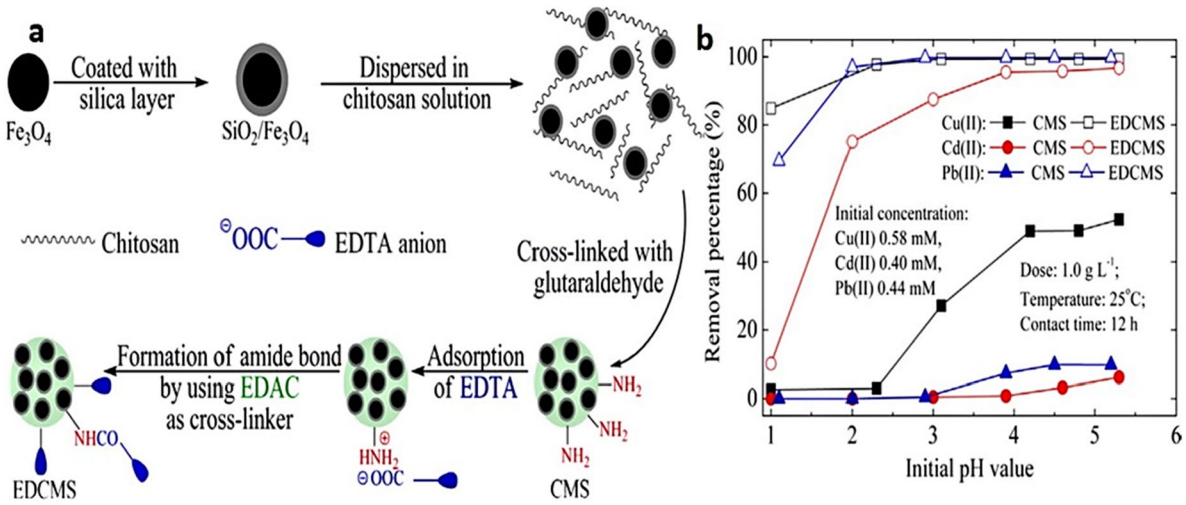


Fig. 8 **a** The procedure for preparation of CMS and EDCMS. **b** Effect of pH on the adsorption of different metals by CMS and EDCMS [62]

an adsorbent material for the removal of Cu(II), Pb(II) and Cd(II) in single- and multi-metal ions system [63]. Zhu et al. developed polyvinyl alcohol (PVA)/chitosan magnetic composite by wet gel method. This composite had an adsorption capacity of 14.39 mg g^{-1} within 2 h, at 97.5% of adsorption. This higher Co^{2+} adsorption value was attributed to the presence of $–NH_2$ and –OH in the composite [64].

Dye Adsorption

Chitin is an abundantly available low-cost bio-polymer for dye removal that can be obtained from natural resources. As compared with other commercial adsorbents, it has received a lot of focus due to its specific properties such as cationic, high adsorption capacity, macromolecular structure, abundance, and low price. Many studies have been carried out based on this advantage of the monomer. Gopi et al. extracted chitin nanowhiskers (ChNW) from shrimp shell and subjected to alkali, bleaching, and acid hydrolysis treatment. This Chitin nanowhiskers (ChNW) synthesized ChNW were used for the adsorption of crystal violet dye from contaminated water. The prepared ChNW showed higher removal efficiency (79.13%) and adsorption capacity of (39.56 mg g^{-1}) which is excellent for an unmodified polymer [65]. Zhu et al. prepared a low-cost alternative composite system by microemulsion process which had an adsorption efficiency of 71.0% towards anionic azo dyes. The study was carried out using methyl orange (MO) and maximum adsorption of MO was obtained at 20 mg L^{-1} within 180 min [66]. Similarly, Soltani et al. prepared a bio-silica/chitosan composite for the adsorption of acid red-88. It was found that the adsorption of Acid Red 88 was proportional to adsorbate concentration, initial pH, decreasing temperature, and reaction time. The adsorption study showed a Langmuir isotherm of the pseudo-second-order kinetic model. The thermodynamic study showed that adsorption is spontaneous and exothermic [67]. Wang et al. developed an antifouling and antibacterial non-woven membrane coated by chitosan combined with glutaraldehyde used as a crosslinking agent which further pretreated by ozone which resulted in the development of carbonyl and carboxyl functional groups in the composite membrane surface. The antibacterial studies using the staining experiment showed that the bacterial adhesion to the composite membrane surface had a significant reduction. The authors proposed a hydrophilization approach as a cheaper alternative for industrial production compared with conventional hydrophobic membranes [68]. Summary of recent works carried by chitin and chitosan for water purification application is illustrated in Table 3.

Biosensors

Chitin and chitosan have two hydroxyls ($–CH_3OH$) and one amino or one acetyl group was widely studied for the preparation of biosensors. The lone pair provides in the amino groups show an affinity towards metal ions and the relatively better compatibility in some aqueous system, these characteristics made chitosan a suitable material for sensor preparation. Casteleijn et al. fabricated chitin-based biosensors by simple spin-coating on, either on gold (Au) or on polystyrene (PS). The approach opens a new area of opportunity because of the soluble property of chitin. The significant chitin-binding observed is evidence for the good performance of the biosensors. The authors also proposed a new surface plasmon resonance surfaces based on copper/zinc oxide for future applications on chitin metal composites with the same metals [75]. Abu-Hani et al. fabricated a highly sensitive low-temperature H_2S gas sensor made of

Table 3 Chitin and chitosan-based composited for water purification application

Composite	Pollutants	Method	Inferences	References
Chitin nanowhiskers	Crystal violet	Chemical modification	The removal efficiency of 79.1% with an adsorption capacity of 39.6 mg g^{-1})	[65]
Chitin nanowhisker-electrospun PVDF membrane	Indigo carmine	Chemical modification with electrospinning	The removal efficiency of 88.9% with an adsorption capacity of 72.6 mg g^{-1}	[69]
Chitin nanowhisker-electrospun PVDF membrane	Oil–water separation	Chemical modification with electrospinning	Filtration performance of 99.1%	[3]
Chitin based fixed-bed column	Fluoride	Copolymerization	Regeneration efficiency of 85%	[70]
Chitin–polypyrrole	Pb(II) and Cd(II)	Copolymerization	Adsorption efficiency of 98.2% and 95.8% against Pb(II), and Cd(II)	[71]
Chitin extracted from crab	Pb(II), Cu(II), Ni(II), Cd(II) and Zn(II)	Unspecified	Maximum adsorption capacities of 50, 47.6, 43.4, 40 and 38.46 (mg l^{-1}) for Pb(II), Cu(II), Ni(II), Cd(II) and Zn(II)	[1]
Thiol-chitin nanofibers	As(III)	Chemical modification	The adsorption capacity of 149 mg g^{-1}	[72]
Acrylonitrile–chitin	As (III)	Radiation-induced grafting	The adsorption capacity of 19.7 mg g^{-1}	[52]
Chitin–humic acid hybrid	Cr(III)	Chemical modification	The adsorption capacity of 10.8 mg g^{-1}	[73]
Chitin and chitosan	Cr(III)	Commercial grades	Maximum adsorption efficiency of 49.9% and 50% against chitin and chitosan	[9]
Chitosan–cellulose acetate	Anionic water pollutants	Solvent casting	Removal efficiency and adsorption capacity of 99.8% and 9.9 mg g^{-1} for acid orange, 99.7% and 9.4 mg g^{-1} for the brilliant yellow	[29]
Chitosan/sulfydrylfunctionalized graphene oxide	Cu(II), Pb(II), Cd(II)	Chemical modification and electrostatic self-assembly	The adsorption capacity of 235, 226 and 117 mg g^{-1} for Cu(II), Pb(II), Cd(II) respectively	[63]
Non-woven chitosan	Microbes, Cr(III)	Electrospinning	The adsorption capacity of 35 mg g^{-1}	[57]
PLA/chitosan nanoparticle	Bacterias	Electrospinning	Antibacterial activity of 99.4% and 99.5% against *E. coli* and *S. aureus*	[2]
EDTA-modified chitosan/SiO_2/Fe_3O_4	Cu(II), Pb(II), Cd(II)	Chemically modified hydrogel	Adsorption capacity of 0.699, 0.596, 0.563 mmol g^{-1} for Cu(II), Pb(II), and Cd(II) ions	[62]
Chitosan-EDTA anhydride	Cu(II)	Chemical modification	The adsorption capacity of 110 mg g^{-1}	[74]
Chitosan/kaolin/γ-Fe_2O_3	Anionic azo dye	Micro-emulsion	The removal efficiency of 71.0%	[66]

conductive chitosan film with the controlled blending of glycerol ionic liquid at various concentrations 1–9% volume/volume (v/v). The resultant composite membrane was a semiconductor with sufficient flexibility and transparency. The sensing mechanism behind the fabricated sensor was the proton transfer between the H_2S gas molecules and the basic amino groups pending from the chitosan chains. Due to the presence of glycerol, the extent of H-bonding formation was increased due to the presence of OH groups. All chemical components in the sensor had high affinity and thereby resulted in high sensitivity. The sensor has the lowest operating temperature of 20 °C with a gas detection limit of 15 ppm with a minimum average response time of 14.9 ± 3.7 s. The sensor had other advantages such as low power consumption, ease of fabrication, transparency and flexibility, etc. [76]. Borgohain et al. developed a similar pollutant sensor for the detection of Zn^{2+} and Cu^{2+} ions in water at various concentrations. They have fabricated chitosan

capped ZnS quantum dot sensors by the co-precipitation technique. Increase in concentration of the metal ions caused aggregation of chitosan capped ZnS QDs small clusters, the clusters formed is proportional to the concentration of metal ions present in the water. This aggrigated clusters results in a shift in absorption peaks towards longer wavelength which could be resulted in lower energy. This change in energy was detected by the UV detector which processed after [77].The mechanism of heavy-metal ion sensor using chitosan capped ZnS quantum dots are shown in Fig. 9. Summary of recent works carried by chitosan for water purification application is illustared by Table 3. Summary of recent works carried by chitin and chitosan for water purification application is illustared by Table 4.

Electromagnetic Interference Shielding

Chitosan possesses many interesting properties biodegradability, biocompatibility, and solubility in aqueous media. The poor mechanical and electrical properties restrict its use in a wider range of applications. This could be overcome by mixing with suitable materials such as clays, hydroxyapatite, metal nanoparticles, and carbon nanotubes. The inherent amphiphilic properties that give a unique capacity to solubilize hydrophobic multiwalled carbon nanotubes (MWNT) in aqueous solution which improved its applicability in EMI shielding application. Liu et al. developed a lightweight graphene/iron pentacarbonyl (IP) porous films with high electrical conductivity, magnetic properties, and excellent EMI shielding properties. They demonstrated that chitosan could optimize the microcellular structure by improving the interfacial adhesion between multiple graphene sheets and pentacarbonyl (IP) flakes along with improvement in electrical conduction within the porous films. This graphene/iron pentacarbonyl porous film structure could shield the electromagnetic radiation of incident microwaves by repeated scattering. The fabricated porous film had a thickness of 0.3 mm with high electrical conductivity of more than 2000 S m^{-1}, excellent broadband EMI shielding performance of more than ~ 38 dB within the X-band. It exhibited EMI shielding performance of more than 40 dB in a very broad frequency range of 8.2–59.6 GHz with a total bandwidth of 51.4 GHz. The lightweight graphene/iron pentacarbonyl (IP) porous films demonstrated in Fig. 10 [86]. Shen et al. fabricated EMI shielding polyester fabrics with carboxymethyl chitosan-palladium coated by electroless nickel plating the surface. To this, Pd^{2+} molecules were adsorbed by a complex adsorption mechanism for fabricating the carboxymethyl chitosan-palladium (CMCS-Pd) complex. The maximum palladium adsorption capacity to the polyester fabrics was calculated as 4.27 mmol g^{-1}. The lowest surface resistance of 125 mΩ sq^{-1} is obtained at maximum polyester fabrics. Thus this composite polyester fabrics had excellent electromagnetic shielding effectiveness of 40–60 dB with more than 96.0% electromagnetic interference cancelled out [87]. Liu et al. fabricated chitosan-MXene (It is a unique family consists of two-dimensional (2D) transition metal nitrides and/or carbides. This is represented by the general formula of $M_{n+1}X_nT_x$ where M represents transition metal, X represents C and/or N and T represents a surface terminating functionality, generally a mixture of –OH, =O, and –F) based composite by vacuum-assisted filtration technique. The fabricated composite had excellent properties while using Ti_3C_2Tx content of 50%. The composite showed a maximum electrical conductivity of 1402 ± 70 S m^{-1} and shielding effectiveness of 15153.9 ± 153 dB cm^{-1} at a thickness of 13 µm. These impressive properties could be attributed to the outstanding metallic conductivity of MXenes

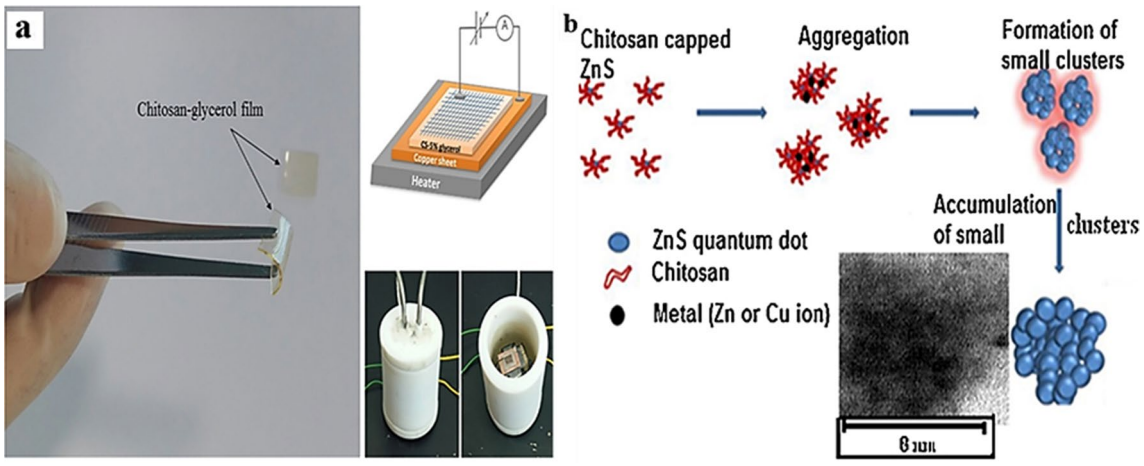


Fig. 9 **a** A representative prepare low-temperature and fast response H_2S gas sensor chitosan–glycerol film [76]. **b** Mechanism of the formation of nanoclusters in the heavy-metal ion sensors using chitosan capped ZnS quantum dots [77]

Table 4 Chitin and chitosan-based composited for biosensor applications

Composite	Sensor	Preparation	Inferences	References
Semiconducting chitosan film	H_2S gas	Casting	The detection limit of 15 ppm, and a minimum average response time of 14.9 ± 3.7 s	[76]
Chitosan/PVP	H_2 gas	Solvent casting	Sensor maximum response of 24% and 46% towards 0.5% and 2% H_2 respectively	[78]
Fe_3O_4/chitosan	Gallic acid (GA)	Chemical modification	The detection limit of 12.1 nM with a dynamic range of 0.5–300.0 µM	[79]
Fe/chitosan coated carbon electrode	As(III)	Co-electrodepositing	The detection limit of 1.12 ppb and 1.01 ppb for mining wastewater and soil respectively	[80]
AgNPs/chitosan-thiourea-formaldehyde	Non-enzymatic glucose	Polymeric metal complexation	The detection limit of 0.046 mM with ultra-high sensitivity of 35.22 mA mM^{-1} cm^{-2}	[19]
F-rGO@CNTs/chitosan	Piezoresistive pressure	Freeze-drying and dip-coating	Sensitivities of 4.97 kPa^{-1} in 0−3 kPa and 0.05 kPa^{-1} in 40−80 kPa and fast response time of 170 ms	[81]
Chitosan/zinc oxide/single-walled carbon nanotube	Chemiresistive humidity	Solution casting	The humidity detection range of 11–97%	[82]
Copper ferrite NP/chitosan	High-performance electrochemical	Ultra-sonication	The detection limit of 8.6 nM with a range of 0.025–697.175 µM	[83]
LSPR based optical fibre/chitosan capped gold nanoparticles on BSA	Hg(II)	Chemical modification	Detection limits of 0.1 and 0.2 ppb for tap water and seawater respectively	[84]
Graphene quantum dots/chitosan	Humidity	Ultrasound dispersion	High response sensitivity (A frequency shift of – 3291 Hz at 95% RH) and Short response/recovery time (36 s/3 s)	[85]

in combination with hydrophily and hydration/dehydration behaviour of the composite paper.

Chitin and Chitosan can be easily modified by many functionalization techniques of both physical/chemical to fabricate desirable composites with good properties for specific applications. These polysaccharide-based materials have shown outstanding sorption for some metals, such as toxic metals (Hg), precious metals (Pd, Pt), and metal anions (Mo and V). The presence of NH^{3+} on the surface also provides an inherent dye adsorption capacity to the material. As mentioned above in this review, the application areas for the chitin and chitosan-based composite are mainly pollutant removal, bio-sensor, and EMI shielding. It was also evident that the use of chitin was not as common as that of chitosan. Recently various patents on chitosan and chitosan-nanocomposite were taken into account related to wastewater purification. There would be great potential for chitosan and chitosan-nanocomposite for the removal of viruses, bacteria, cryptosporidium oocysts, and giardia cysts in the bio-medical related areas and removal of soluble and insoluble organic pollutants, polyaromatic hydrocarbons and heavy metals from wastewater.

Energy Applications of Chitosan-Based Composites

Chitin and chitosan-based composite in various forms having various structures possess a set of physicochemical properties that uniquely equips it for hierarchical assembly of nano-scale components for range applications. The stimuli-responsive film/gel-forming properties which enable these polysaccharides to self-organize at the nano/micro scale has been shown a significant material science value and application potential in many energy-related fields. Even though with major similarities in microstructure, the applicability of chitin is inferior to chitosan which is evident by the number of research works that's have been carried out. Some of the most common applications are mentioned below.

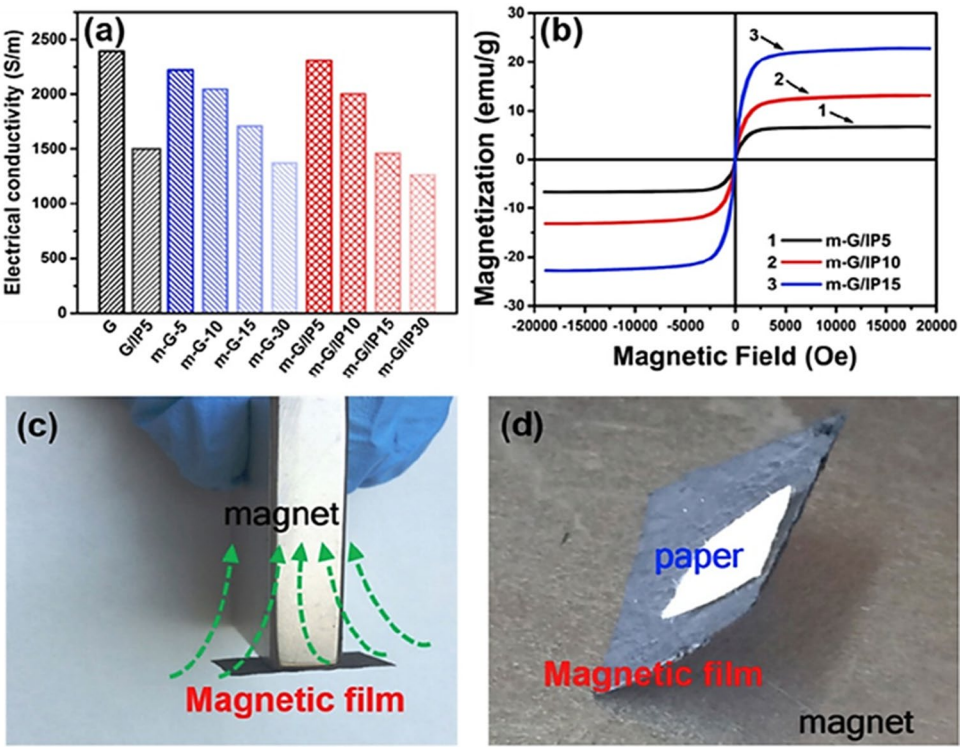


Fig. 10 Conductive and lightweight graphene/iron pentacarbonyl porous films in **a** Electrical conductivities of graphene and its derivative films; **b** Hysteresis loops of m-G/IP porous films; **c**, **d** Digital images showing the magnetic property of m-G/IP5 porous films [88]

Fuel Cell

Fuel cells based on proton exchange membranes are an excellent substitute for environmentally friendly energy sources which give rise to excellent new features making them worthy of further researches. Developing a sufficient proton-conducting membrane is the most significant factor determining the overall performance of the fuel cell itself. Li et al. developed a microbial fuel cell by anaerobic degradation of chitin by *aeromonashydrophila*. The fabricated microbial fuel cell claimed to have seven-fold higher chitin degradation to that of a fermentation system, which thereby resulted in additional electricity generation. This work provides an efficient degradation of recalcitrant biomass to recover energy which itself is an additional advantage [89]. He et al. engineered a chitosan and graphene-based homogenous, highly porous scaffold by ice segregation induced self-assembly method for bio-anode of high performance in a microbial fuel cell. The immersion process in liquid nitrogen resulted in the formation of sponge-like 3D scaffolds with impressive shape recovery properties. This arrangement provided space inside the anode for bacterial colonization, this multi-layered bacterial arrangement and biocompatible vacuum-stripped graphene improve the electron transfer process in the fuel cell. This porous architecture in combination with the anode material selection could have resulted in the maximum power density improvement of 78 times [90]. Liu et al. developed a chitosan/silica-coated carbon nanotube composite by a simple sol–gel method for preparing proton exchange membranes for fuel cell applications. The silica-coated carbon nanotubes (SCNTs) provide additional advantages such as the low risk of electronic short-circuiting and enhanced interaction between SCNTs and chitosan which ensured the homogenous dispersion of SCNTs. The composite exhibited an improved thermal and oxidative stability, improved proton conductivity and mechanical properties compared with the pure chitosan membrane. The maximum proton conductivity value reported was 0.025 S cm^{-1} this was mainly due to the electrostatic interactions and hydrogen bonding between SCNTs and chitosan which would help to form the continuous ion-transporting channels while the lower proton conductivity was explained by lower water uptake due to reduction in theamino functional groups [91]. Vijayalekshmi et al. developed methanesulfonic acid and sodium dodecylbenzene sulfonic acid doped chitosan-based green polymer electrolyte which is cross-linked, flexible, oxidatively, and thermally stable. The polymer electrolyte had conductivity up to 4.67×10^{-4} S cm^{-1} at 100 °C with a maximum with thermal and oxidative stability up to 260 °C. This low cost and eco-friendly synthesis method with decreased methanol uptake at higher methanol concentration ensure better methanol barrier property which is schematically represented in Fig. 11 [92]. Summary of recent works carried out using chitosan for fuel cell applications is illustrated in Table 5.

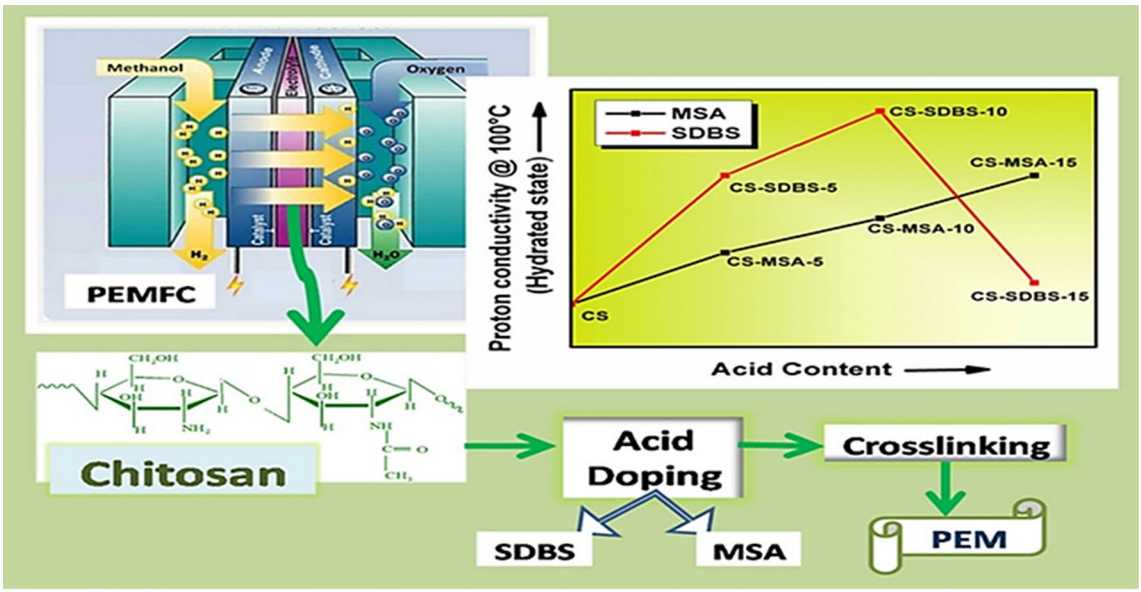


Fig. 11 Eco-friendly methanesulfonic acid and sodium salt of dodecylbenzene sulfonic acid doped cross-linked chitosan-based green polymer electrolyte membranes for fuel cell applications [92]

Table 5 Chitin and chitosan-based composited for fuel cell applications

Composite	Ionic conductivity, S cm^{-1}	Methanol permeability, cm^2 s^{-1}	References
Carbon nanotube modified quaternized chitosan/polyvinyl alcohol	4.7×10^{-2}	10.7×10^{-7}, 2 M methanol + 5 M KOH, 80 °C	[93]
Chitosan/montmorillonite/Nafion	$4.5–8.3\times10^{-2}$, 95% R.H., 25 °C	$0.57–1\times10^{-7}$, 25 °C	[94]
Chitosan-based triple-layer proton exchange membrane	8.8×10^{-2}, 95% R.H., 25 °C	2.52×10^{-7}, 25 °C	[95]
Organophosphorylated titania–chitosan	1.14×10^{-2}, 25 °C	2.8×10^{-7}, 2 M MeOH	[96]
Organophosphorus acids/PVA/chitosan	3.59×10^{-3}, hydrated, 30 °C	2.41×10^{-7}, 5 M MeOH	[97]
Phosphonic acid–chitosan	$2.48–4.29\times10^{-2}$	$0.49–1.03\times10^{-7}$, 30% MeOH	[98]
Chitosan sulfate membranes	3.1×10^{-2} at 80 °C	4.7×10^{-7}, 2 M MeOH	[99]
Chitosan—glutaraldehyde–sulfosuccinic acid	4.52×10^{-2}, hydrated, 25 °C	9.6×10^{-7}, 25 °C	[100]

Supercapacitors

Supercapacitors are new energy storage devices having high capacitance, high power density with long cycle durability, higher stability with exceptional electrochemical properties. Due to these outstanding performances, many studies have been devoted to developing these materials from sustainable resources. Hao et al. developed a high-performance supercapacitor from chitosan by a three-step process. The steps include aerogel formation, carbonization of aerogel, and nitrogen self dopping process. The process introduced both macro and mesopores in the graphene framework and amorphous carbon in the system. At a very high activation temperature, the amorphous carbon could be faded completely to form stable graphene which resulted in a framework by complete removal of amorphous carbon by etching. This composite had a claimed specific capacitance of 197 F g^{-1}at 0.2 A g^{-1} with maximum capacitance retention around 92.1 after 10,000 cycles. The fabricated supercapacitors had achieved major significant performance values such as a high energy density of 27.4 W h kg^{-1} and a maximum power density of 20 kW kg^{-1} [101]. In another work, Cao et al. developed a chitosan-based supramolecular hydrogel via an ultrafast hydro-gelation process where they cross-linked chitosan and Ag^+ within two seconds. This combined with fast-mobile Li^+ ions resulted in a supramolecular hydrogel of solid-state electrolyte with good capacitance values of 10 mF cm^{-2} at the 1.8 mA cm^{-2} with survivability more than 10,000 cycles. This technique have inferior properties but the fast and simple technique is a novel approach that covered all the basic requirements of being a supercapacitor up to a certain extend which has great potential to be discovered as per the authors which are demonstrated in Fig. 12 [102]. Summary of recent works carried out using

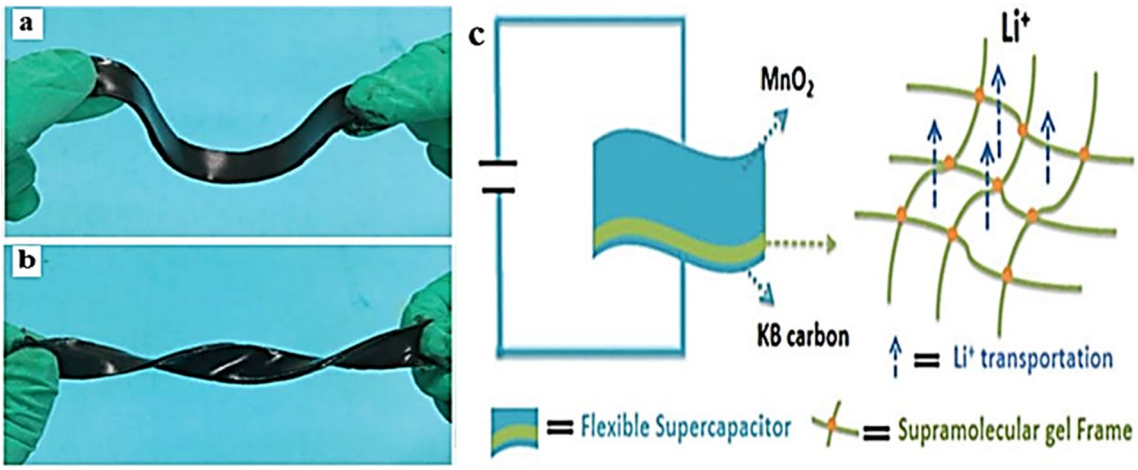


Fig. 12 **a**, **b** Demonstration of the flexible supramolecular supercapacitor. **c** Schematic representaion flexible supercapacitor on a chitosan supramolecular gel frame [102]

chitin and chitosan for supercapacitor applications is illustrated in Table 6.

Solar Cells

Chitosan is the only amino-containing polysaccharide with abundant availability since it is the second most abundant

Table 6 Chitin and chitosan-based composited for fuel cell applications

Composite	Fabrication	Inference	References
Polypyrrole/chitin nanofibers/carbon nanotubes	Vacuum filtration with freeze-drying	The specific capacitance of 362 F g^{-1} at 5 mV s^{-1} in 1 mol L^{-1} Cycling stability with retention of 86.6% after 5000 cycles at 2 A g^{-1}	[103]
Chitin/graphene oxide/zinc oxide/polyaniline	Co-polymerisation	The specific capacitance of 543 F g^{-1} at 0.1 A g^{-1}	[104]
Cellulose acetate/chitosan/PVA gel	Phase inversion and Dip polymerizing	The conductivity of 7.1 9×10^{-2} S cm^{-1} The capacitance of 5.5 mF cm^{-2} at 20 mV s^{-1} and capacitance retention of 71.2% after 1000 cycles	[105]
MOF-5/chitosan	Chemical modification	The specific capacitance of 199.9 F g^{-1} and rate capability of 75.6% from 0.05 to 4 A g^{-1}	[106]
Polyionic liquid/carboxymethyl chitosan (nitrogen- and sulfur-codoped porous carbon)	Direct carbonization	The specific capacity of 633 F g^{-1} at 0.1 A g^{-1} Cycle stability have a low loss after 10,000 cycles	[107]
Carbon nanotube/chitosan-ferrocene	Chemical modification and drop coating	The specific capacity of 695 F g^{-1} at 0.1 A g^{-1} Cycle stability retained up to 99.93% after 2000 cycles	[108]
Zn–iron oxide/grapheneoxide/chitosan	Solution mixing evaporation	The specific capacity of 830 Fg^{-1} at 0.1 A g^{-1}	[109]
Carbon nanofibers/chitosan/cobalt nanoparticles	Digestion	The specific capacity of 438.6 Fg^{-1} at 0.1 A g^{-1} Capacitance retention of 95.6% after 5000 GCD cycles	[110]
CuO decorated graphene oxide/chitosan	One-pot chemical precipitation method	The specific capacity of 772.3 Fg^{-1} at 0.2 A g^{-1}	[111]

biomass on earth after cellulose. The amine groups on chitosan main chain made it as a promising candidate for using it in cathode interlayer, adding to it, the hydroxyl and amino groups along its main chain allow further functionalization. The chitosan can form transparent film while having net canonicity had attracted great attention among scientists for developing solar energy-based cells. Zhang et al. developed a series of organic solar cells using Layer-by-Layer (eLbL) self-assembled chitosan with uniform and controlled thickness in the nanometer-scale which exhibited a maximum power conversion efficiency of 10.18%. The higher efficiency of the solar cell was attributed to the ordered layer-by-layer structure which could be resulted in both interfacial and molecular dipoles. These dipoles were utilized to decrease the work function of the electrode which could be contributed in enhanced device performance. The self-assembled chitosan interlayer exhibited a power conversion efficiency of 9.34% which was roughly 200% higher to that of the cell with no cathode interlayer and 100% better compared to spin-coated chitosan interlayer. This organic solar cell is schematically demonstrated in Fig. 13 [112]. Buraidah et al. developed a high performance plasmonic dye-sensitized solar cell using chitosan-based polymer electrolyte. The chitosan-based solar cell had polyethene oxide (PEO) sandwiched between the TiO_2/dye photoelectrode and the Pt counter electrode. The ion donor NH_4I was introduced by a simple solution casting method to this system. The compositions of 16.5 wt% chitosan–38.5 wt% PEO–45 wt% NH_4I exhibited an increase in conductivity since the blending of chitosan with PEO increases the electrolyte's flexibility, ions mobility resulting in increased conductivity. The dye-sensitized solar cells (DSSC) prepared using red cabbage extract dye exhibited the maximum short-circuit current density (J_{sc}) of 0.31 mA cm^{-2}, which had the highest open-circuit voltage (V_{oc}) of 0.39 V with an efficiency of 0.06%. The blueberry extract dye-sensitized solar cells exhibited relatively lower values of J_{sc} and V_{oc} of 0.27 mA cm^{-2} and 0.34 V respectively. The overall efficiency also improved from 0.06 to 1.13% (19 times) by incorporating TiO_2 particles to the cell system [113].

Lithium-Ion Battery

Chitosan with abundant hydroxyl and amine groups as an additive for cathodes and separators has been proven to be an effective polysulfide trapping agent in lithium-sulfur batteries. Chai et al. reported chitosan as an effective binder for spherical graphite anode-based lithium-ion battery. The fabricated battery had superior columbic efficiency, cycling behaviour, and rate capability compared to the conventional polyvinylidene fluoride (PVDF) binder. The chitosan-based binder exhibited a columbic efficiency of 95.4% compared to 89.3% efficiency of PVDF based binder. They found that capacity retention of chitosan-based binder exhibited a significant difference after 200 cycles when compared to the conventional PVDF binder [114]. Prasanna et al. carried out a similar study using chitosan-based binder where they have achieved superior properties such as a higher discharge capacity of 159.4 mAh g^{-1} with a significantly higher capacity retention ratio of 98.38%. The common PVDF binder only had discharge capacity and capacity retention ratio of 127.9 mAh g^{-1} and of 85.13% respectively and this is shown in Fig. 14 [115]. Zhong et al. fabricated conductive and water-soluble carboxymethyl chitosan-based binder which was used in combination with poly-3,4-ethylene dioxythiophene and polystyrene sulfonate to promote the conduction

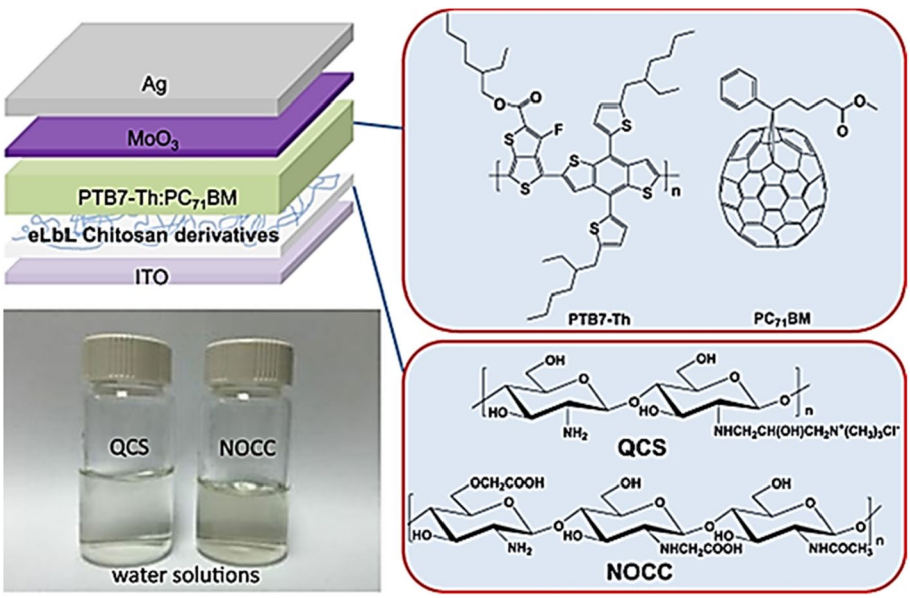


Fig. 13 Device configuration of an inverted organic solar cell and the chemical structure of chitosan derivatives working as efficient cathode interlayers for organic solar cells [112]

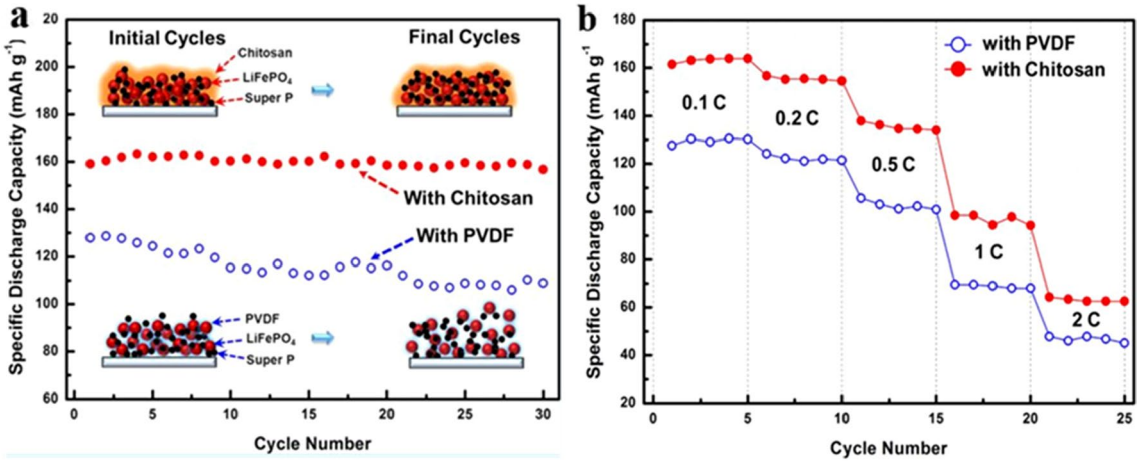


Fig. 14 **a** Schematic diagram of chitosan-based binder in Li-ion battery. **b** Specific discharge capacity of chitosan-based and PVDF based binders [115]

in lithium-ion batteries. After 1000 cycles, the carboxymethyl chitosan-based binder exhibited around 98% retention capacity compared to 95.4% retention capacity of commercial PVDF based binder [116]. Summary of recent works carried out using chitin and chitosan for lithium-ion battery applications is illustrated by Table 7

Application of chitosan-based composite materials has been proved to be an effective approach for developing a much eco-friendly, low-cost alternative to the conventional synthetic energy appliances especially considering the overall net-cationic charge, low cost, ease of processibility and abundant availability. The recent advancement in energy demand with sustainable materials facilitated the need for the development of chitosan for various applications such as lithium-ion batteries, fuel cells, supercapacitor, and fuel cells have given greater perspective. From the last 20 years, there is a significant interest in developing these materials as a successful counterpart to the conventional synthetic energy appliance. Several inspiring works have been initiated for the utilization of chitosan for using it as a polymer electrolyte membrane and electrode in fuel cells. This could lead to a new wave of energy-related research with chitosan-based materials as most of the properties of chitosan can be tailor-made by deacetylation and functionalization techniques.

Overall Summary

Application of chitin and chitosan-based composites have been proved to be effective for developing much eco-friendly, low-cost alternative to the conventional synthetic energy appliances especially considering the overall net-cationic charge, low cost, ease of processability and abundant availability. The recent advancement in energy demand with sustainable materials facilitated the need for the development of chitosan for various applications such as lithium-ion batteries, fuel cells, supercapacitor, and fuel cells have given greater perspective. From the last 20 years, there is a significant interest in developing these materials as a successful counterpart to the conventional synthetic energy appliance. Several inspiring works have been initiated for the utilization of chitosan for using it as a polymer electrolyte membrane and electrode in fuel cells. This could lead to a new wave of energy-related research with chitosan-based materials as most of the properties of chitosan can be tailor-made by deacetylation and functionalization techniques.

Table 7 Chitin and chitosan-based composites in fuel cell applications

Composite	Fabrication	Inference	References
Chitin nanofiber from prawn shell/sodium dihydrogen citrate (SDCA)	Chemical extraction and vacuum drying	The stable discharge capacity of ~ 157 mAh g^{-1} over 15 cycles	[117]
Chitin fiber non-woven separator	Centrifugal jet-spinning	Stable discharge at a current of ± 200 µA	[118]
Nitrogen-doped carbon /chitosan/cellulose nanocrystal	Casting	Maximum specific capacity 383 mAh g^{-1} at 100 mA g^{-1} Cycling stability 327 mAh g^{-1} after 50 cycles	[119]

Conclusions and Prospects

Chitin is the most widespread amino polysaccharide and is the second natural polysaccharide after cellulose. Chitin and chitosan are biopolymers of polysaccharide groups with excellent structural possibilities for chemical and mechanical modifications to create novel properties, functions, and applications, especially in the biomedical area. Due to the abundant nature of chitin and chitosan across the globe, biorenewability and the fast-growing technologies on its production, chitin, and chitosan are becoming the main focus of product development and research as observed from the numerous researches published on chitin and chitosan for the last couple of years. In this context, it is foreseeable that in nearby future, chitin and chitosan will be extensively found in many areas since they could be tailor-made for various specific applications in energy and environmental sectors, food, biotechnology, medical, electronics industries, etc. Also, chitosan itself and chitosan-based nanomaterials are amazing materials that have a wide range of promising applications. The functionalize surface facilitates the easy blending with other materials which improves the physicochemical properties. The abundant nature along with their specific properties may lead to many sustainable promising products and these fore mentioned products could be scalable at an industrial level which gives a promising green and sustainable future. Despite its enormous availability, the use of chitin has been limited by its intractability and insolubility. Their derivatives that are soluble in aqueous media have the unique properties of chitin as film-forming polymer, with biodegradable, renewable, antibacterial, and fungistatic properties. Because of limits like high cost, hard chemical modification, etc., the applications of chitin are limited to the biomedical and pharmaceutical industry, with cosmetics in second place. Chitosan, which is water-soluble in acidic media, or under specified conditions at neutral pH, is the most important derivative of chitin. The difficulty to get reproducible initial polymers is one of the limits of chitosan. The advantage of chitosan over other polysaccharides is that its chemical modification is feasible. In this review, applications of chitin and chitosan polymers for energy and environmental applications have been extensively reviewed. Major fundamental technological advances have been utilized to enhance the capabilities and improve the properties and reliability of chitosan and chitosan nanomaterials for different applications especially for energy and environmental applications. These emerging applications are a standing testimony to the multifaceted roles played by the chitin and chitosan composites in various applications. Considering the potential and promising nature of both chitin and chitosan, these biopolymers can be employed for a wider range of applications in the nearby future, particularly with the current environmental concerns. Additionally, the greener EMI shielding materials based on chitin and chitosan would occupy the telecommunication sector in nearby future especially with the current boom that we see nowadays. We also expect similar trends to carry on towards engineering and defence sectors as these sectors are more performance and results-driven. However, these biopolymers have shown a promising alternative to synthetic materials for functional applications in various industries in the nearest future, especially in environmental safety concerned related aspects. As chitin and chitosan have to gain immense interest from both academia and industries, a rapid development in its production utilizing the upgraded technology will be achieved to provide better comprehension and more applications, thus stepping further from laboratory to the commercial market. With new inspirations suggested by novel characterization of chitosan and chitosan-based nanomaterials and vast innovative opportunities brought by nanotechnology, it is reasonable to expect the significant advances that will revolutionize the nanotechnology field very soon.

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