Nanochitin for Sustainable and Advanced Manufacturing

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Abstract

Presently, the rapid depletion of resources and drastic climate change highlight the importance of sustainable development. In this case, nanochitin derived from chitin, the second most abundant renewable polymer in the world, possesses numerous advantages, including toughness, easy processability and biodegradability. Furthermore, it exhibits better dispersibility in various solvents and higher reactivity than chitin owing to its increased surface area to volume ratio. Additionally, it is the only natural polysaccharide that contains nitrogen. Therefore, it is valuable to further develop this innovative technology. This review summarizes the recent developments in nanochitin and specifically identifies sustainable strategies for its preparation. Additionally, the different biomass sources that can be exploited for the extraction of nanochitin are highlighted. More importantly, the life cycle assessment of nanochitin preparation is discussed, followed by its applications in advanced manufacturing and perspectives on the valorization of chitin waste.

Keywords: Chitin, Nanomaterials, Sustainability, 3D Printing, Photonic, Catalyst

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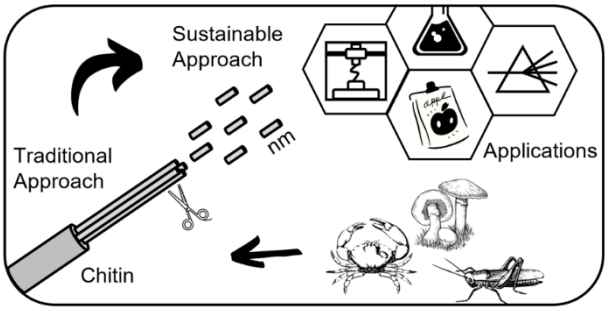

Among the numerous strategies to synthesize nanochitin from the waste, the more sustainable methods are identified to facilitate the valorization of chitin wastes and its eventual infiltration into the advanced manufacturing

1 Introduction

The amass of 6-8 million tons of crustacean wastes annually[1] presents an issue of inefficient resource utilization where these valuable resources instead of being tapped on to produce value-added products, are being disposed and create the problem of waste accumulation. This increasing waste pile up is in stark contrast to the prevailing climate of being sustainable. In the alignment to the goals of sustainability and circular economy, coupled with the advantages of chitin, much research efforts have therefore been devoted to valorizing it.

Chitin discovery can be dated back to 1811. After more than a century of investigation and exploration, various approaches have been developed to extract/process chitin into different scales, and chitin is ready to be employed in various applications. (**Fig. 1a**). As a linear polysaccharide composed of β(1→4)- linked 2-acetoamido-2-deoxy-β-D-glucose, chitin is the second most abundant renewable biopolymer found in the world after cellulose. Given its abundance, it is not surprising that chitin is further classified as either α, β or γ. The main difference between the three types lies in the alignment of the molecular chains.[2] If the molecular chains are in antiparallel fashion, it is known as α-chitin, whereas parallel molecular chains are considered as β-chitin.[2] γ-chitin is made up of both parallel and antiparallel molecular chains. α-chitin is the more stable form and it exists as the backbone of crustacean and insect exoskeletons as well as the cell walls of microorganisms.[2] β-chitin, in contrarily, can be found in squid pen, tubeworms and cuttlefish bone[2] whereas γ-chitin in some cocoons and mushrooms.[3] Chitin sparks the interests of researchers with not just being abundant and affordable, but it can also impart toughness and resistance to the materials.[1] Through adjusting its concentration, the toughness and resistance of the materials can be varied and tightly regulated to serve the intended purpose. Furthermore, chitin has many other attractive benefits such as biodegradability, low allergenicity, biocompatibility and easy processability.[1]

Nanochitin is structurally made up of a bundle of semicrystalline chitin nanofibrils that are held together by van der Waals forces and hydrogen bonding.[1] It usually exists together with protein and minerals. Hence, it is necessary to deproteinize and demineralize to isolate nanochitin. To date, researchers have explored various forms of nanochitin such as nanocrystal and nanofiber.[4] Through breaking down chitin to nanoscale dimension, the reactivity of the chitin can be preserved while its solubility/dispersibility can be improved[1, 5] and used in a wider scope of applications. Nanochitin is an attractive polymer as it is the only natural polysaccharide that contains nitrogen, which can serve as a natural nitrogen source to produce nitrogen containing chemicals, e.g. compounds used in pharmaceuticals.[6] As an elemental building block of chitin, nanochitin also possesses the advantages of chitin such as toughness, easy processability and biodegradable etc. Additionally, the acetamide group presents on the nanochitin endows it with antimicrobial activities, non-toxicity and wound-healing ability.[3] While there are increasing publications per year on nanochitin, it still lags its parent chitin (**Fig. 1b**). Nevertheless, the attention on nanochitin is picking up at an increasing rate over the years as illustrated by the growing citations (**Fig. 1c**).

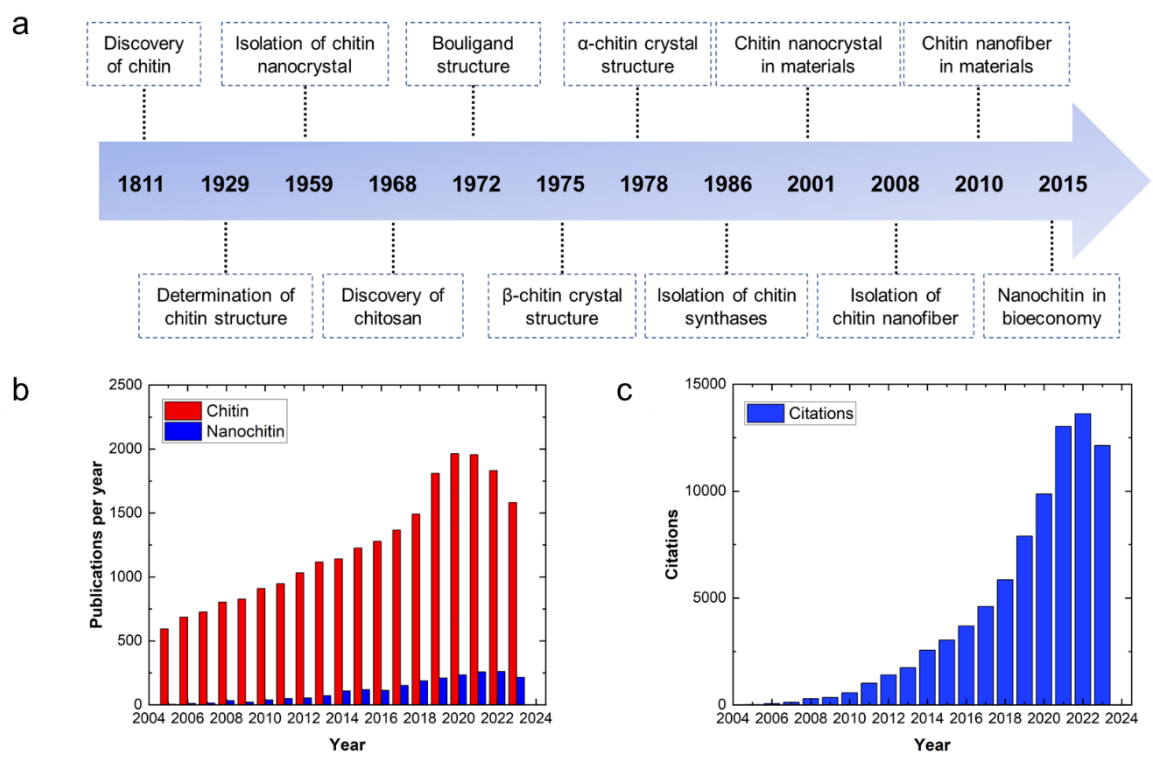

Fig. 1 (a) Timeline of chitin and nanochitin from its discovery to analysis and applications. Adapted with permission.[1] Copyright 2022, American Chemical Society. (b) Annual publications on chitin and nanochitin from 2005 to 2023 (c) Annual citations on nanochitin from 2005 to 2023. The data is obtained from Web of Science, 14th December 2023.

The review is structured in a way to provide readers with the knowledge of the various existing methods to synthesize nanochitin. These methods are usually categorized into chemical and mechanical treatments. In contrast, we summarized the recent approaches in a new light by further grouping them into either traditional or sustainable to aid researchers to push the frontier of sustainable research. Different sources of biomass that can be tapped into for the extraction of chitin are highlighted. While the valorization of crustacean wastes, specifically chitin, into value added products is desirable to achieve circular economy, the environmental impact from cradle to grave is attempted with life cycle assessments to present the true benefits of the valorization. The review ends off with a whole range of applications

that nanochitin can be utilized in such as in the arena of, 3D printing, photonic, packaging and catalysis follows by a perspective on the sustainable use of nanochitin.

2 Biomass Sources for Chitin

Chitin is traditionally sourced from the seafood industry, where the exoskeletons of crustaceans such as shrimps, crabs and crawfish are discarded as wastes.[7] In order to diversify the future sources of chitin, other forms of supplies are also studied. In general, chitin exists in three types of polymorphs (**Fig. 2**); α-chitin is the main isomorph present in the exoskeletons of crustaceans and molluscs, β-chitin are found in squid pens, while γ-chitin exists in cocoon fibers of *Ptinus* beetles.[4] These polymorphs differ in the stacking arrangement of the polymeric chitin chains. Due to this difference, the degree of H-bonding interactions from the amide functional groups between the polymeric chains would differ and thus exhibit different properties. In particular, α-chitin and β-chitin contain polymeric chitin chains that are stacked in anti-parallel and parallel configurations, respectively. On the other hand, γ-chitin consists of both anti-parallel and parallel arrangements of the chitin chains. Generally, chitin has been extracted and studied from three groups of sources: aquatic invertebrates, insects, and fungi.[8] The extraction process generally involves demineralization (acid treatment), deproteinization (alkaline treatment) and decolorization steps. All these treatments will need to be optimized according to the chitin source due to the differences in physicochemical properties.

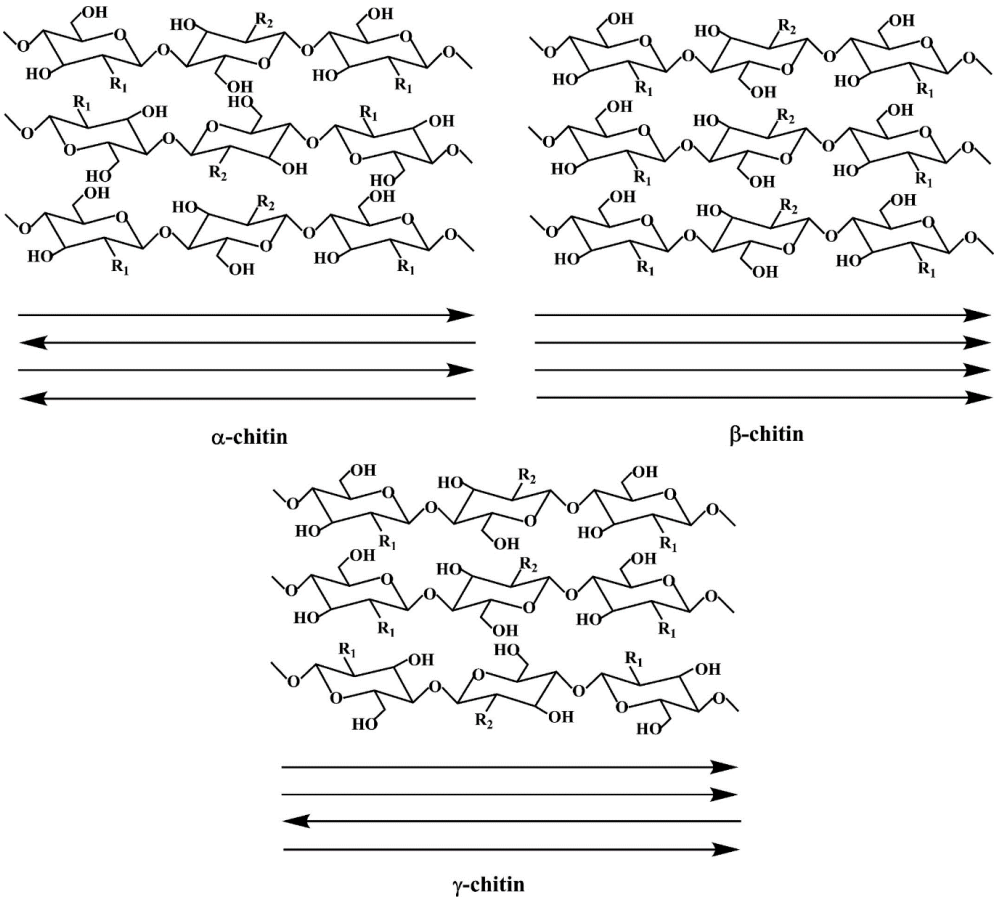

Fig. 2 Schematic illustrations of the three types of chitin polymorphs. Reproduced with permission.[9] Copyright 2020, John Wiley and Sons.

2.1 Aquatic Invertebrates

Aquatic invertebrates, such as crustaceans, molluscs and cephalopod, represent an important food source globally. In particular, the exoskeletons of crustaceans, which are also major waste products in the seafood industry, have been extensively studied as a source of chitin.[10] Presently, they are the primary sources of commercially produced chitin.[7] More specifically, shrimp shells are more commonly used as the source of chitin due to a thinner exoskeleton, which made chitin extraction easier than other forms of shells. Generally, the crustacean shells are harder and more brittle than the other chitin sources due to a well-connected network between the chitin, minerals and proteins. Therefore, the chitin extraction process is harsher, which requires crushing and concentrated acids for adequate

demineralization. Milder chemical or enzymatic treatments have also been proposed, though this approach is still not widely adopted in the industry. Crustacean shells generally comprise of chitin (20-30%), proteins (30-40%), inorganic minerals (30-60%), and lipids (0-14%).[11] These compositions vary significantly across species and seasons.

Rajeevgandhi and his team studied the chitin extraction from various crustacean shells, i.e. crab, lobster, shrimp and squilla.[12] Utilizing the traditional chemical treatments for chitin extraction, the chitin yields from the four types of crustaceans amounted to 21.25%, 17.50%, 20.00% and 23.75%, respectively. As presented in **Fig. 3a**, the surface morphologies of the extracted chitin differed from the sources. Shrimp and crab chitins exhibited porous structures at low magnifications and nanofibrous structures at high magnifications. Squilla chitin showed the opposite characteristics, while lobster chitin mainly displayed nanofibrous structures. Considering that the surface structures could affect the potential functionalities of the nanochitin, it is thus important to choose the right chitin source. The authors also found that the chitin obtained from this work has a low molecular weight, which is classified as those below 50 kDa. In general, chitin with low molecular weight is desired for chemo-drug delivery applications.

2.2 Insects

There has been a growing number of industrial farms that produce insects as a new source of protein for feed and food.[13] Considering that insects contain chitin, insect farms can thus be a potential continuous source of chitin. Furthermore, exoskeletons of insects contain less inorganic minerals than the shells of crustaceans, thus the yield of chitin could be potentially higher while the chitin extraction process could also be milder.

Huet and colleagues investigated the extraction of chitin from *Bombyx eri* larvae.[14] The authors highlighted that the chitin contents in the cuticles of larvae and the shells of shrimps

were 45% and 19%, respectively. Furthermore, the mineral content in the studied insect chitin was significantly lower than that in shrimp chitin (1.9% vs 21.7%). Therefore, it is theoretically possible to achieve higher chitin yield and a milder required extraction process from this insect source. The authors demonstrated this feat by obtaining a chitin yield of 31.1% with a purity of 89.9% via a single-step extraction process without undergoing demineralization. With the same extraction process applied to shrimp shells, chitin yield was 17.1% with a purity of less than 65.0%.

Black soldier flies (BSFs), *Hermetia illucens*, are one of the most studied insects as feed. This is largely due to the species' ability to thrive on various organic streams, especially manure and food wastes. In addition, the byproducts formed at various lifecycle stages of the insects contain chitin. Soetemans et al. studied the extracted chitin at different stages of lifecycle of BSFs, namely the larvae, sheddings, prepupae, pupae, cocoons and flies (**Fig. 3b**).[15] All of these chitin samples were found to be mainly composed of α-chitin, similar to shrimp chitin. Among them, sheddings were the most difficult to purify (75.7%) even though it exhibited one of the highest chitin contents. This could be attributed to a higher mineral content, which requires a harsher extraction process. On the other hand, cocoons of BSFs were identified to possess a high chitin content of 24% and the extracted chitin exhibited crystallinity index and purity of 94% and 97%, respectively. Nonetheless, the authors concluded that the various chitin samples had generally minor differences in the physicochemical properties, thus it is still possible to perform a convenient homogeneous chitin extraction process with all chitin-containing byproducts at once.

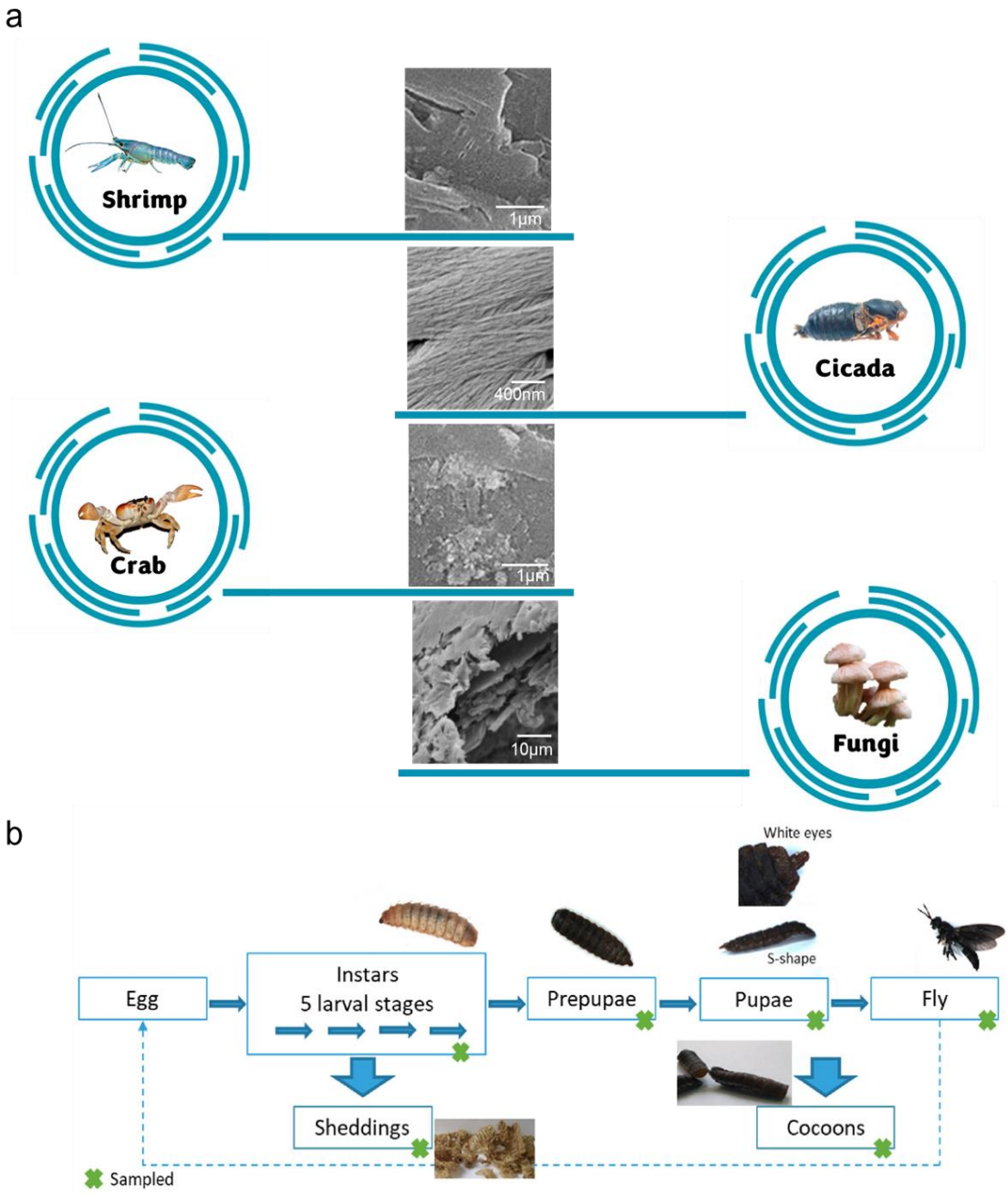

Fig. 3 (a) SEM of chitin from various sources. Adapted with permission.[12] Copyright 2021, Elsevier Ltd. [16] Copyright 2016, Elsevier Ltd. [17] Copyright 2023, Elsevier B.V. (b) Investigation of chitin extraction from various life stages of BSF. Reproduced with permission. [15] Copyright 2020, Elsevier Ltd.

2.3 Fungi

Chitin is also present as the major polymeric component within the cell wall of certain groups of fungi, e.g. Ascomycetes, Basidiomycetes, Deuteromycetes, Zygomycytes, etc.[8] In fact, chitin was first isolated from a fungus source by Braconnot in the early 1800s. Although fungi generally contain lower chitin content as compared to crustaceans (10–26%), fungi chitin is attracting an increasing academic and commercial attention. Fungal-based chitin is advantageous over animal-based chitin due to an absence of inorganic minerals, a more uniform composition, an abundance in non-seasonal availability and represent as a vegan source.[18] However, the chitin in fungi exists as a component of a network with other polysaccharides, for e.g. cellulose, mannan, glucan, etc., thus complicating the chitin extraction process. Specifically, chitin and β-glucan are associated via covalent bonds. Therefore, a chitin-β-glucan complex is commonly obtained after performing the alkaline treatment on fungi sources (without demineralisation step). In order to obtain pure chitin from this complex, acid treatments are required to selectively degrade the glucan components.[19]

Due to the species-richness of fungi, one can expect the properties of the extracted chitin to vary considerably. Vetter investigated the chitin content of various cultivated edible mushrooms (*Agaricus bisporus*, *Pleurotus ostreatus* and *Lentinula edodes*).[20] Saprotrophic *A. bisporus* contained higher chitin composition (6.7–8.8%) than other two mushrooms (2.2–8.1%). Bamba et al. showed that α-chitin nanofibrils from microalgae *Phaeocystis globosa* had comparable tensile strength as those extracted from squid pens and tubeworms.[21] Considering that spent biomass produced during fermentation, such as the production of citric acid, studies had also been conducted to investigate the chitin content of *Aspergillus niger*.[22] The yield of the extracted chitin-β-glucan complex was 44% with a good chitosan content of more than 32%.

Table 1 Summary of selected examples of chitin sources

Source	Chitin yield (%)	Properties	Reference
Crab (shells)	21.3	Porous, nanofibrous	[12]
Lobster (shells)	17.5	Nanofibrous	[12]
Shrimp (shells)	20.0	Porous, nanofibrous	[12]
Squilla (shells)	23.8	Nanoporous, fibrous	[12]
Bombyx eri larvae (cuticles)	31.1	No demineralization required	[14]
Black soldier flies (cocoons)	24.0	High crystallinity and purity	[15]
Mushroom *A. bisporus*	6.7–8.8	Higher chitin level in the pileus (cap)	[20]
Microalgae *Phaeocystis globosa*	-	Nanofibrils with high tensile strength	[21]
Aspergillus niger	44.0%	Exists as chitin-β-glucan complex	[22]

3 Nanochitin Fabrication

In the preparation of nanochitin, there are usually two main steps involved. It starts with the purification step of the chitin which primarily involves; i) deproteinization using alkali or enzyme hydrolysis, ii) demineralization achieved by using acid and iii) removal of lipids and pigment using bleaching treatment. Then, the purified chitin can be attained in either dry or wet state for further processing.[23, 24] The subsequent step to attain nanochitin (i.e. nanocrystals and nanofibers) comprises of the microfibration method of the purified chitin and the various methods to achieve it can be categorized into either traditional approach or sustainable approach. **Fig. 4** illustrates the various methods for nanochitin preparation.

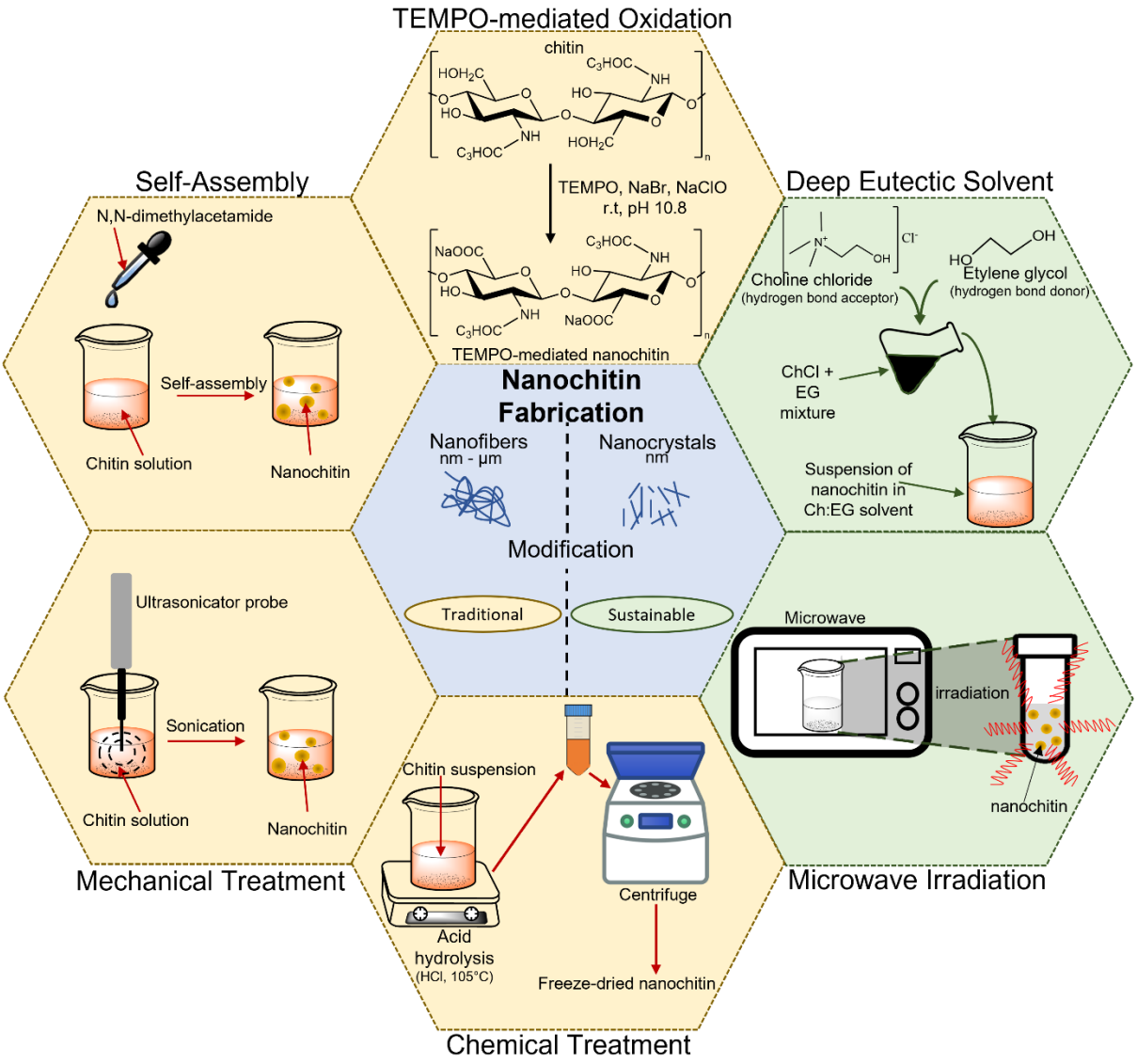

Fig. 4 The various types of nanochitin synthesis

3.1 Traditional Approach

The reliance on chemicals, mechanical disintegration, electrospinning, wet spinning and self-assembly methods to obtain nanochitin are considered as the traditional approaches. They are either the earliest methods developed for nanochitin extraction or the methods that emphasize efficiency and yield. These techniques can be further classified into top-down (i.e. chemical treatment, mechanical treatment, TEMPO mediated oxidation) or bottom-up approaches (i.e. electrospinning, wet spinning, self-assembly method). In the former, the

synthesis of nanoparticles is performed by breaking down the bulk material whereas in the latter, it is created from small building blocks.

3.1.1 Chemical Treatment

Acid hydrolysis has been widely explored as an effective method to attain nanochitin. In the acid hydrolysis process, the acid attacks the amorphous region of the chitin in which the macromolecular chains are packed in a disordered, low lateral ordered arrangement.[25, 26] As a result, the chitin chains are cleaved transversely along the amorphous regions, leaving high crystalline domains intact and forming nanochitin with a rod-like appearance.[27] Chitin nanowhiskers were created by Marchessault in 1959 by the acid hydrolysis of chitin using 3M hydrochloric acid (HCl) while illustrating the liquid behaviour of these nanocrystals.[28] To effectively hydrolyze the chitin, Revol and his colleagues increased the temperature of acidified suspension to its boiling point and agitated it.[29] The reaction was quenched by adding distilled water, and the suspension was centrifuged or filtered to remove the acid solution. The suspension was then dialyzed to neutral pH using distilled water to completely remove the presence of residual acid and stored for further use. While the acid hydrolysis technique involves the use of strong acid solution such as hydrochloric acid (HCl) or sulphuric acid (H_2SO_4), it was realized that the crystalline region of chitin completely dissolves as the acid concentration increases beyond 8.5N.[28] Since the discovery, numerous studies have attempted this acid hydrolysis method (ranging from 2.5 to 3M HCl, 1.5 to 6 h hydrolytic time) on various sources of chitin (squid pen[30], riftia tubes[31], crab shells[32, 33], and shrimp shells[34, 35]) to produce nanochitin of length varying from 50 to 600 nm, and widths between 8 and 50 nm.

For instance, Zhenya and colleagues effectively isolated the crystalline region of the nanochitin from shrimp chitin powder using HCl hydrolysis and obtained rod-like nanoparticles with a length of 50-150 nm and width of 30-50 nm.[36] Similarly, Zhou et al. also

extracted nanochitin from shrimp chitin powder and obtained a slender rod with sharp points with a broad distribution of 100-150 nm in length and 15-30 nm in width.[37] Qin and team replaced HCl with H_2SO_4 to produce nanochitin and attained size ranging from 100 to 400 nm in length and 10 to 50 nm in width.[38] This procedure enables sulphate half-ester functionalities to be present at the nanochitin surface. It is undeniable that acid hydrolysis is effective in generating nanochitin. The handling of corrosive chemicals and the generation of wasteful effluents however are undesirable and in fact, detrimental with respect to sustainable development.

3.1.2 Mechanical Treatment

Another strategy that has been extensively utilized in the nanochitin synthesis is the application of mechanical force. The mechanical treatment involves a high shear force which initiates transverse cleavage along the longitudinal axis of the chitin microfibrillar structure, that are held together by hydrogen bonds, and isolates the nanochitin fibers.[39-41] Grinding and ultrasonication are some of the few examples of mechanical treatment techniques that can be used separately or in combination with other treatment techniques such as acid hydrolysis to produce nanochitin.

The grinding process involves breaking down the hierarchical structure by using shearing forces produced by two countersense rotating grinding stones.[42] For the chitin to be effectively fibrillated during the grinding process, an acidic environment is required. This is because a small percentage of amino group in chitin becomes cationized when acid is added, which aids the fibrillation of chitin through electrostatic repulsion.[43] A study was conducted to compare the chitin nanofibers obtained from 1% slurry of crab shell chitin that was passed through a grinder with and without acetic acid.[44] It was found that due to the strong hydrogen bonding between chitin networks, it is challenging to fibrillate chitin without the presence of

acid, leading to a formation of large, dense bundles of chitin nanofibers. Although an acidic environment is necessary for the grinding process to create chitin nanofibers, this condition may not be ideal for certain production of nanocomposites, electrical devices, and biological materials. Hence, Ifuku and team have attempted to produce chitin nanofibers via grinding under neutral condition, and they succeeded in extracting chitin nanofibers from prawn shell chitin with a consistent diameter of around 10-20 nm.[43]

Ultrasound is another popular technique that is used for producing nanostructured materials where the high energy generated causes the process of formation, growth, and rapid collapse of cavities in water.[45] Cavitation typically produces energy between 10 to 100 kJ/mol which is equivalent to the energy level of hydrogen bonds.[46] Therefore, the formation of chitin nanoparticles due to ultrasonication process is by rupturing the strong hydrogen bonds between the network of chitin. Lu and colleagues extracted chitin nanofibers from dried prawn shells chitin using high intensity ultrasonication method at an optimal parameter of 60kHz, 300 W and in pH 7.[47] The extent of breakage of weak Van der Waals forces and hydrogen bonding within the fibers was found to vary with the ultrasonication duration, which allows the diameter of chitin nanofibers to be controlled between 20 to 200 nm. The results showed that after 30 minutes of sonication, high-aspect-ratio nanofibers were obtained with a consistent width of 19.4 nm.

3.1.3 TEMPO-Mediated Oxidation

An extensively studied and yet expensive method, utilizes a typical piperidinenitroxide free radical known as 2,2,6,6-tetramethylpiperidine-1-oxide (TEMPO). The -OH groups at the C6 position of chitin can be selectively oxidized to C=O groups in the presence of TEMPO/co-oxidation system giving rise to chitin nanofibers. Yimin and colleagues have developed a method utilizing TEMPO-mediated oxidation to selectively oxidize the amorphous region of

chitin through the radical oxidation pathway.[48] Basically, several steps are involved in this technique: (i) chitin is suspended in water containing TEMPO and sodium bromide (NaBr) before sodium hypochlorite (NaClO) solution is added to begin the TEMPO-mediated oxidation of chitin. (ii) sodium hydroxide (NaOH) is continuously added to maintain the pH at 10 at room temperature. (iii) to stop the oxidation process, ethanol is added to the solution without using any alkali.[49] In a study, β-chitin isolated from tubeworms was subjected to TEMPO/NaClO/NaBr oxidation at pH10 to produce chitin nanofibers with a width ranging 20-50 nm and a length of over few microns.[50] It was found that increasing the amount of NaClO caused the length of chitin nanofibrils to become shorter. Most of the β-chitin was oxidized to carboxyl groups and transformed into water-soluble sodium chitin salt when adequate amount of NaClO was added. Similar observation was noted in another independent study in which higher NaClO concentrations resulted in shorter chitin nanofibrils, potentially caused by the intensification of the depolymerization reaction at the ends of the chitin nanofibrils.

Chitin can only oxidize by the TEMPO/NaClO/NaBr system in an alkaline environment. For the first time, Pang and team successfully produced chitin nanofibers with a width of 5-10nm and a length of 200-400 nm by employing TEMPO/NaClO2/NaClO system under mildly acidic environment.[51] They suspended chitin in a pH 6.86 sodium phosphate buffer solution containing TEMPO, sodium chlorite ($NaClO_2$) and NaClO to produce chitin nanofibers via oxidation reaction. A similar TEMPO technique with acidic conditions was used by Jiang et al. to create chitin nanocrystals with dimensions of 200-600 nm in length and 6-15 nm in width.[52]

3.1.4 Deacetylation pretreatment

Fan and team produced chitin nanocrystals using a different approach and it involves mechanically treating partly deacetylated chitin fibrils at low pH [53]. The partly deacetylated

chitin fibrils would consist of increased C2-primary amino groups on the crystal fibers surface. This would lead to a greater number of cationic charge density from the protonation of the amino groups which therefore stabilize the dilute colloidal dispersion of chitin nanowhiskers due to enhancement of electrostatic repulsion between the fibrils. In an acidic environment, this repulsion aids the chitin fibrils disintegration during mechanical process and produces chitin nanocrystals. The acid-degraded chitin dispersion may also experience an isotropic-anisotropic nematic transition when dewatered to an increased concentration [54]. In this method, three primary steps involved which are: i) the partial deacetylation of chitin step – chitin was added and stirred in 33% (w/w) NaOH solution that consist of $NaBh_4$ and heated at 90 °C for 1-4 hours to prevent alkaline depolymerization and weight loss. After that, the chitin solution was centrifuged to neutralization after being rinsed several times with distilled water; and ii) undergoes mechanical disintegration step – the chitin solution was adjusted to pH 3-4 by using acetic acid solution and vigorously stirred for 5 days and finally; iii) the sonication step – the mixture was exposed to a minute sonication by using ultrasonic homogenizer. Junfei et al. have utilized this method to prepare partially deacetylated α-chitin nanofiber from crab shell flakes to formulate high strength membranes with nanocellulose and F-SiO_2 suspensions [55]. The approximate width of nanochitin was between 10 nm to 20 nm whereas the length fell within the range of 400 to 600 nm.

3.1.5 Electrospinning

The electrospinning technology enables the production of uniformly sized, long nanofibers. In electrospinning, a high voltage is placed between a conductive plate and a tiny aperture which a solution or polymer melts travels to produce a non-woven mat of fibers.[56] The only way to prepare chitin nanofibers using bottom-up approach is via electrospinning and different chitin concentrations have varying impact on the formation of electro spun nanofibers.[57] Chitin is insoluble in most solvents such as water, organic solvents, acidic and

alkaline solution and can only dissolve in 1,1,1,3,3,3-hexafluoro-2-pro-panol (HFIP).[58] According to Street et al., chitin was dissolved in HFIP solution and electrospun at optimum conditions (17kV voltage, 1.0mL/h flow rate, 21% relative humidity, 23℃ temperature and 10cm distance between tip and the collector).[59] It was found that the tensile strength of nanofibers increased by 30% by using electrospinning method compared to randomly collected fibers. However, HFIP is highly toxic, which restricts its use in electrospinning. Therefore, to enhance chitin solubility, it is advisable to lower the molecular weight by utilizing methods such as Co60 gamma ray, microwave irradiation, and ultrasonic treatments. To increase chitin solubility, Min et al. depolymerized chitin using a Co60 gamma ray before dissolving it in HFIP solution for electrospinning. The obtained chitin nanofibers achieved a diameter ranging from 40 to 640 nm and an average diameter of 110 nm.[60]

3.1.6 Wet Spinning

Wet spinning is another example of a dissolution-regeneration method which involves dissolving chitin and then using it as a precipitating agent to regenerate chitin molecules into nanofibers. To produce nanochitin fibers with high aspect ratios, it is possible to use wet spinning method and the spinning effect depends on the chitin concentration. According to the experimental findings, chitin solutions with higher concentrations gelled more quickly compared to lower concentrations where it coagulated too slowly for spinning.[61] Additionally, the wet spinning approach may be utilized to spin chitin composites solutions as well as pure chitin solutions.[62, 63] Wet spinning, however, has restricted applications due to the limited solvents for chitin. To fully exploit wet spinning for the generation of chitin nanofibers, it is crucial to develop environmentally friendly solvents that dissolve chitin.

3.1.7 Self-Assembly

The self-assembly method may also be used to create nanochitin, which allows solvents to easily dissolve chitin by rupturing its hydrogen bonds before it regenerates into nanofibers. [64] Example of solvents used are 1-Allyl-3-methylimidazolium bromide (AMIMBr), sodium hydroxide/urea, hexafluoro-2-propanol (HFIP) and N,N-dimethylacetamide (DMAC). In a study, two different solvents (HFIP and LiCl/DMAC) were used to dissolve chitin to produce nanofibers. Chitin dissolved in HFIP solution produced nanofibers with a 2.8 ± 0.7 nm diameter using solvent evaporation technique whereas chitin dissolved in LiCl/DMAC solution produced nanofibers with 10.2 ± 2.9 nm diameter by the precipitation of the fibers with water. [65] According to Duan et al., chitin nanofiber microspheres were created via a thermally induced self-assembly process in a NaOH/urea solution.[66] Commonly, urea hydrates surround the NaOH hydrogen-bonded chitin complex to create a water-soluble sheath-like structure which causes the chitin to dissolve. However, high temperature destroys the urea-NaOH sheath that leads to vigorous aggregation of the chitin chain in parallel manner and results in the formation of nanofibers with an average diameter of 27 nm.

3.2 Sustainable Approach

Increasing occurrences of extreme weather, global warming and rising water levels have attracted plenty of attention and growing pressure is faced to either find sustainable means or to bear the consequences of the unsustainable development. Nanotechnology is not an exception as researchers sought to improve and achieve a cleaner and more environmentally friendly process. Up to present, different approaches for nanochitin synthesis have been attempted ranging from employing more environmentally friendly processes, using greener solvents to accelerating the reaction to save energy, which will be delved into more details in this section.

3.2.1 Microwave Irradiation

Microwave irradiation technique is a sustainable approach to extract nanochitin. The technique involves the polar solvent sample to be exposed to the electromagnetic field and the dipoles of the molecules from the sample would attempt to align themselves which results in friction and collisions leading to an increase in the temperature.[67] Fernández-Marín et al. described using the microwave irradiation approach to manufacture nanochitin from chitin obtained from shrimp, lobster, and squid. Both lobster and shrimp samples produced rod-shape-like nanochitin with shorter lengths and widths compared to nanochitin from squid samples that have long, fibrillar structures.[68] By using microwave-assisted extraction, reaction time can be reduced. For instance, depending on the chitin source, the time may be reduced to 10-30 mins as opposed to the 90-180 mins needed for conventional chemical acid hydrolysis and the HCl concentration can be lowered from 3M to 1M.

3.2.2 High Pressure Homogenization

High pressure homogenization is a procedure that exerts intense pressure on the suspensions and separates them into smaller size particles.[69] High pressure homogenization is a straightforward and environmentally friendly technique used by Salaberria et al. to extract chitin nanofibers from yellow lobster chitin.[70] This procedure involves chitin suspension to be ejected at high pressure via a homogenizing valve which effectively reduces the size of chitin nanofibers under 100 nm in diameter and several micrometers in length.[70] Chitin nanofibers have recently been produced from chitin isolated from raw crustacean exoskeletons using an atomizing technique known as the high-pressure waterjet (HPWJ) system. Aqueous counter collision (ACC) method and Star Burst method are the two techniques that use the HPWJ system. In the ACC technique, the chitin suspension is passed through a set of nozzles at 50-270 Mpa pressure and produced a set of jets.[71] Hence, adjusting the pressure and the number of ejecting steps would result in repeated collisions of the sample that would reduce the size of the chitin particles in the sample. Kose and Kondo produced chitin nanofibers of 10-20 nm

width from chitin powder using this technique.[72] Ishida et al. synthesized chitin nanofibers with an average width and length of 10 ± 6 nm and 2300 ± 1000 nm, respectively by using nano-pulverization process with an ACC system of 200Mpa pressure and 60 passes of ejecting steps.[73] The Star Burst technique involves compressing the chitin slurry by hydraulic piston which is then passed through a nozzle at high pressure (245Mpa) and the chitin is atomized by colliding with a ceramic ball within the chamber.[74] By using the Star Burst method, Aklog and team successfully synthesized chitin nanofibers from chitin extracted from red snow crab shells (*Chionoecetes opilio)*.[75] The chitin slurry was ejected through a 100 μm diameter nozzle, under high pressure of 200 Mpa and this was repeated for 1, 5, 10, 30, and 50 cycles. After the first cycle, the chitin slurry was already slightly fragmented and nanofibers could be detected which was attributed to the high mechanical load. The width of the fibers can be reduced by increasing the number of ejecting steps that brought about repeated fibrillation of the nanofibers bundle of chitin.

3.2.3 Ionic Liquids

Ionic liquids (IL) are viewed as environmentally friendly salts which melt below 100℃ and are made completely of anions and cations.[76] These substances have been suggested as an alternative to organic and aqueous solvents for the dissolution and swelling of biomass. These ILs solutions containing chitin could be used to create chitin nanofibers via electrospinning method. In a study conducted, the chitin isolated from raw crustacean shells were dissolved by the ionic liquid 1-ethyl-3-methylimidazolium acetate, which was used to spin immediately into fibers and films. Many researchers used similar methods to produce chitin nanocrystals where chitin was first gelated with AMIMBr, then it was regenerated with methanol. More specifically, the resultant gel was briefly immersed in methanol and then sonicated to create a suspension of chitin nanocrystals. In a study, chitin nanocrystals with dimensions of 20-60 nm

in width and several 100 nm in length were produced and utilized as a suspension to create a film by filtration method.[77]

3.2.4 Deep Eutectic Solvent

Deep eutectic solvent (DES) is known as a form of green solvent that consists of high, nonsymmetric ions with low lattice energy and hence low melting point. A quaternary ammonium salt or hydrogen bond acceptor (HBA) and a metal salt or hydrogen bond donor (HBD) are often complexed to produce DES.[78] This complexation causes charge delocalization through hydrogen bonding which aids to decrease the melting point of the mixture.[78] DESs have always been misunderstood and referred to as ILs analogs due to their similarities to ILs such as high solvent capacity and low vapor pressure. However, DESs are less expensive, more accessible, non-toxic, recyclable, biodegradable and easier to produce than ILs.

Sharma and team were the first to report that by using conventional heating, microwave heating, and ultrasound-assisted heating, α -chitin could be dissolved in DESs in a 1:2 mole ratio for the mixture of choline chloride:thiourea, choline chloride:urea, chlorocholine chloride:urea, choline bromide:urea, and in a mole ratio of 1:4 for betaine hydrochloride:urea.[79] A year later, Mukesh and colleagues used the same DESs mole ratio mixture as Sharma et al. [79] for choline chloride:thiourea and produced chitin nanofibers with a width of 25-45 nm and a length of 162-450 nm.[80] Similarly, chitin nanocrystals were created with a range of 42 to 49 nm diameter and a length of 257 to 670 nm by utilizing choline chloride and various acids such as lactic acid, oxalic acid, citric acid, malonic acid, and DL-malic acid in a ultrasound-assisted procedure (**Fig. 5**).[81]In a different investigation, a green, non-volatile solvent of DES containing choline chloride:zinc chloride with a mole ratio of 1:2 was employed to produce acetylated and esterified chitin nanocrystals in a one-step synthesis.[82] Chitin nanocrystals with

high yield (≈88.5%) was produced from betaine chloride:ferric chloride hexahydrate mixture with a molar ratio of 1:1.[83]

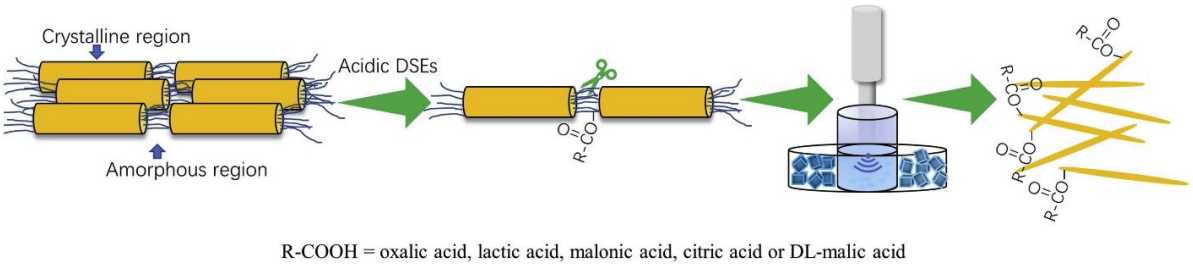

Fig. 5 Illustration of nanochitin synthesis using organic acid DESs. Reproduced with permission.[81] Copyright 2020, Elsevier Ltd.

3.2.5 Enzymatic hydrolysis

When compared to chemical synthesis approach, biological approaches using a range of microorganisms are viewed to be more environmentally friendly. Though biological approaches are likely to be the greenest isolation method, the efficiency and cost remain to be improved. Using this technique, nanochitin could be easily obtained by simply incubating the chitin with the enzymes followed by stopping the reaction with either heat or ice and isolating the purified nanochitin. A recent study involved Barandiaran et al. incubating the α-chitin flakes with lytic polysaccharide monooxygenase (LPMO).[84] The mixture was put on ice to halt the reaction upon completion. The nanochitin isolation was performed by using ultrasonication, centrifugation and lyophilization. After seventy-two hours of incubation, the nanochitin obtained had length and diameter of 458 nm and 32.3 nm respectively. The cleavage site was figured to be the β-(1 → 4) glycosidic bond, where C1 and C4 were selectively oxidized. In another study, chitinase was used along with ultrasound to prepare nanochitin fibers.[85] Upon completion of the reaction, heat was applied to the mixture to stop the reaction. The purified nanochitin was obtained after ultrasonication and lyophilization were applied to the mixture. The results are promising with the length of the attained nanofibers varied from 130 nm to 195

nm depending on the duration of the enzymatic hydrolysis. Other factors that could affect the efficacy of the enzymatic hydrolysis include the environmental environment and the enzyme concentration.

Table 2: The table below shows a summary of the sources, preparation methods of nanochitin

Type of Nano chitin	Typical source	Formation process	Characteristics			Application	Reference
			Length/nm	Width/nm	Diameter/nm		
Nanocrystals	Shrimp	Acid hydrolysis, ultrasound	300	60	-	Films for food coating and packaging	86
Nanofibrils	Crab	Acid hydrolysis, homogenization, ultrasound	150-200	5-10	-	Antimicrobial film for packaging	87
Nanocrystals	Cuttlefish bone	Acid hydrolysis, ultrasound	22	14	-	-	88
Nano whiskers	Rifia Tubes	Acid hydrolysis, ultrasound	500-10^4	18	-	Nanocomposite films	31
Nanofibrils	Tubeworm, pens of squid	TEMPO-mediated oxidation	several microns	20–50	-	Translucent gel	50
Nano whiskers	Crab shells	TEMPO-mediated oxidation, ultrasound	150-500	20-55		For fuel cell applications	89
Nanofibers	Chitin powder	Electrospinning method	-	-	163	For wound healing and regeneration of oral mucosa and skin.	90
Nanofibers	Chitin powder	Electrospinning, Co^{60} gamma ray, deacetylation	-	-	40-640	Nanofibrous matrices	60
Nanofibers	Crab shell	Ultrasound	650	9-120	-	Textile industry for antibacterial finishing application	91
Nanofibers	Crab shell	Grinding	-	10–20	-	Nanomaterials	44

Nanofibers	chitin powder	Grinding, HPWJ treatment	-	-	-	Nanofibrous matrices	[40]
Nanocrystals	Crab shell	TEMPO-mediated oxidation, partial deacetylation, Starburst	250	15	-	Zwitterionic nanocrystals for biomedical field	[49]
Nanocrystals	shrimp shells, squid pens, yellow lobster	Acid hydrolysis, Microwave irradiation	314-900	41-42	-	-	[68]
Nanowhiskers	crab shell	Partial deacetylation	250	6.2	-	Nano-composite materials for reinforcement	[53]
Nanofibers	Chitin powder	Self-assembly	-	-	2.8-10.2	Nanofibrous matrices	[64]
Nanocrystals	Shrimp shells	Deep eutectic solvent	100-700	20-80	-	-	[82]
Nanofibers	Shrimp shells, practical grade chitin powder, pure chitin powder	Ionic liquid	-	-	-	Film for medical application	[92]
Nanofibers	Chitin powder	Dissolution-regeneration			3×10^4-9×10^4	Nonwoven mat for wound dressing	[61]
Nanofibers	Crab shell	TEMPO-mediated oxidation, aqueous counter collision	492-828	-	-	Hydrogel with enhanced mechanical properties for various application	[71]
Nanofibers	Shrimp fragment powder	Partial deacetylation, high-pressure homogenization	400-600	10-20	-	Waterproof packaging, waterproof transparent membrane	[55]
Nanocrystals	Chitin powder	Enzymatic hydrolysis	458	-	32.3	For biomedicine such as tissue engineering and bioprinting	[84]
Nanofibers	Crayfish shell	Enzymatic hydrolysis, ultrasound	130-195	-	-	For emulsions	[85]

3.3 Sustainable Analysis of Nanochitin Extraction

Globally, energy and environmental concerns have reignited scientific interest in the development of materials derived from biomass, which are more sustainable than materials derived from fossil fuels. Apart from demonstrating desirable functionalities, performing life cycle assessment (LCA) for nanochitin is necessary to quantify the sustainability of the nanobiopolymer.[93] LCA is an established methodology to evaluate the environmental impact of the technology of interest from cradle to grave. The process to perform LCA involves three general steps (**Fig. 6**). First, the scope of the study needs to be defined, which includes the boundaries and limitations. Second, the quantitative inputs (energy, resources, chemicals, etc.) and outputs (emissions/wastes to the environment) during the life cycle of the processes involved will be modelled. Lastly, the impact analysis is conducted by converting the model data to interpretable environmental impacts, which are categorized into midpoint and endpoint indicators. Midpoint indicators focus on the short-term impacts, such as climate change, terrestrial acidification, water depletion, etc. On the other hand, endpoint indicators focus on the long-term eventual impacts, such as damages on human health, ecosystems and resource availability.

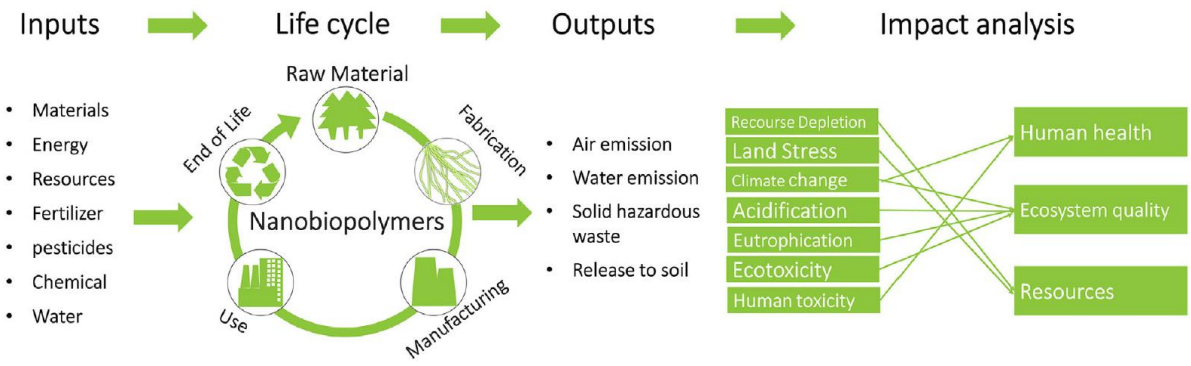

Fig. 6 A general process of LCA for nanobiopolymers, such as nanochitin. Reproduced with permission.[93] Copyright 2018, John Wiley and Sons.

Generally, there are various factors that can affect the environmental impact score of the technology.[93] First, the raw material determines the chitin content and thus the extent of chemical treatment required. At the same time, the raw material determines the resource availability and accessibility. Second, the isolation techniques of nanochitin can have different levels of impact, for example, replacing the use of concentrated hydrochloric acid (HCl) and sodium hydroxide (NaOH) would reduce the environmental impact. Third, the manufacturing of nanochitin-based products has various extents of impact, which differs greatly according to the applications (biomedical, agricultural, catalysis, etc.). LCA is necessary to quantify the relative impacts of each factor. Presently, most of the reported nanochitin production processes are still at low technology readiness levels (TRL), hence no comprehensive LCA has been conducted on this nanomaterial yet. Nonetheless, there are some reported LCAs that are relevant to provide a useful reference point for future studies.

Muñoz and co-workers presented a cradle-to-gate LCA of the production of bulk chitosan, which is derived from chitin via an additional deacetylation process.[94] This study assessed the primary data from two producers located in India and Europe that produce chitosan for general purposes and medical use, respectively. As these two chitosan productions involve different supply chains, production locations and different uses, it was expected that they would have distinct environmental profiles. For the Indian-produced chitosan (**Fig. 7a and 7b**), the major impact of chitin production (from shrimp shells) on climate change and acidification was related to the use of HCl and the ammonia emission from the use of protein-rich sludge as fertilizer. The HCl and NaOH treatments also exert significant impact on ecotoxicity and water quality. For the European-produced chitosan (**Fig. 7c and 7d**), chitin (from crab shells) was sourced and produced from China. As coal was the main fuel used for heating and electricity in China, energy generation was identified as the main contributor to the impact on climate change, acidification and ecotoxicity. Notably, the acquisition of crab shells for chitin

production had resulted in a credit in the acidification impact indicator as the crab shells were diverted from being composted, thus ammonia and NO_x emissions were avoided. This avoidance in acidifying emissions was actually more significant than the emissions associated with the production of chitin, i.e. a net reduction of acidification could be achieved through chitin production. This work highlighted the important factors that could contribute to the global environmental impacts for chitosan (and thus chitin) production, hence providing a useful benchmark for future investigations, though there would be some differences for chitin production in nanoscale.

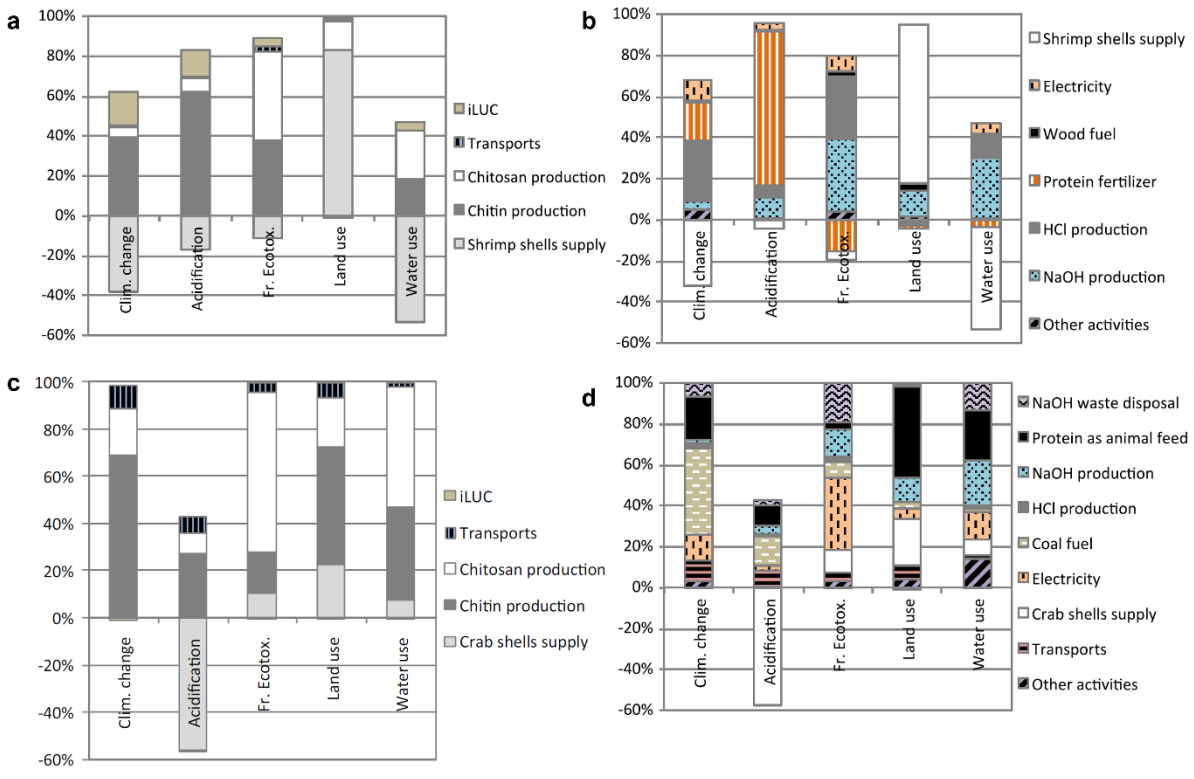

Fig. 7 Impact assessment disaggregated into individual activities for the chitosan production in (a,b) India, and (c,d) Europe. Reproduced with permission.[94] Copyright 2018, Springer Link.

Cinelli et al. conducted a LCA study for a bio-plastic based on polylactic acid and chitin nanofibrils (CNF).[95] For the analysis of CNF production, the energy associated to the concentrating process of CNF suspension, i.e. drying of water, was the main factor affecting

the overall evaluation. The authors suggested the direct production of concentrated CNF suspension of 20 wt% (vs the original 2 wt%) to avoid the energy-intensive purification step. However, additives will be further required to aid the dispersion of CNF in the concentrated suspension, which may cause a change in bio-plastic properties or require additional steps to remove the additive present at a later process stage. Alternatively, one could also explore the use of less energy-intensive separation methods, such as membrane filtration to concentrate the CNF suspension. It is important to note that this LCA is specifically for the production of CNF-containing bio-plastics, therefore the requirement for the preparation of concentrated CNF suspension may not be applicable for other nanochitin materials with different applications.

As the production of nanochitin advances to a higher TRL, it will be increasingly crucial to evaluate the ecological footprint of these emerging materials through comprehensive LCAs. Additionally, LCA will be an important tool to provide a quantifiable justification for the sustainable chitin production from alternative sources (crustaceans vs insects vs fungi).

4 Nanochitin Applications towards Advanced Manufacturing

Advanced manufacturing can be defined as the adoption of innovative or cutting-edge technology in production, either to improve the process or the product. The reduction of chitin to the nanoscale has seen the emergence of an ingenious technology. In the nanoscale form, nanochitin gains new properties such as higher reactivity that arises with higher aspect ratio and new interaction with light. Apart from the new gained advantages, nanochitin still maintains the attributes as its predecessor which makes it attractive for uses in various sectors ranging from 3D printing, photonic to packaging and catalysis. This section summarizes the recent works on nanochitin in each field.

4.1 Nanochitin for 3D Printing

Nanochitin has gained popularity recently in three-dimensional (3D) bioprinting applications. 3D bioprinting is a method of additive manufacturing that utilizes biocompatible

filaments that may or may not be cell-laden to produce complex, tissue-like constructs by layer-by-layer deposition.[96, 97] Nanochitin provides biocompatibility and biodegradability to 3D bioprinted constructs used in regenerative medicine and tissue engineering. The high aspect ratio of nanochitin allows it to enhance the mechanical strength of objects constructed using bioinks, making nanochitin an attractive candidate as a filler in bioinks.[98, 99]

Karimipour-Fard et al. synthesized a nanocomposite filament of polycaprolactone (PCL) matrix with nano-hydroxyapatite (n-Hap) and ChNW fillers using a 1-Butyl-3-Methylimdazolium chloride (BMIMCl) ionic solvent. Preosteoblast mouse bone cell line was used to investigate the applicability of the nanocomposite filament for tissue engineering. It was found that ChNW increased the mechanical properties and the biodegradation rate of the PCL/n-Hap/ChNW filaments as well as enhanced the cell attachment and proliferation.[100]

Sadhasivam et al. fabricated a nanocomposite filament of poly(butylene adipate-co-terephthlate) (PBAT) and nanochitin filler for injection moulding. Similarly, nanochitin improved the thermal and mechanical properties of the PBAT/nanochitin filament, with optimum composition being 30% nanochitin. 3D constructs made from the PBAT/nanochitin filament were stable and expected to be biodegradable. The PBAT/nanochitin nanocomposite was shown to promote cell migration in a scratch wound assay and exhibited *in vivo* non-toxicity in a Zebrafish embryo model.[101]

Melo et al. developed a bioink consisting of nanochitin and alginate (Alg), where the viscosity of the bioink could be controlled by changing the concentration of nanochitin. The swelling properties of the Alg/nanochitin bioinks were also improved by the addition of nanochitin and stable 3D structures could be printed using Alg/nanochitin bioinks with 2.7 wt. % nanochitin.[102]

In another study, Zhang et al. designed an *in situ* self-assembling bioink made of fumed silica (FS) and nanochitin for 3D printing. Nanochitin enabled the FS/nanochitin bioink to display the mechanical, viscoelastic, and rheological properties required for 3D printing. 3D objects printed with the optimal concentration of 5-8 wt. % nanochitin in the bioink possessed high structural fidelity and the ability to support their own weight after extrusion. 3D scaffolds printed using this FS/nanochitin bioink were elastic and could return to their original shape after being subject to multiple deformations.[103]

4.2 Nanochitin for Photonic Applications

Native photonic chitin structures can be found in natural occurring species such as crustaceans and insects.[104] Due to the periodic ordered chitin exoskeleton, the chitin micro/nano-structure interacts with light selectively and displays bright iridescent colors.[105, 106] To mimic such photonic structures, scientists explored the use of the exoskeleton of such creatures as a template for replication (**Fig. 8**).

Multiple research work has utilized butterfly wings as a bio-template for in-situ growth of metal nanoparticles. Boruah et al. deposited sliver ions (Ag^{+}) into the chitin layers of a *Pieris Brassicate* butterfly wing and subsequently converted them into sliver (Ag) nanoparticles.[107] The wings were soaked for varying duration and their photonic band gap was studied. The band gap opening is determined by the interactions between localized surface plasmon of Ag nanoparticles and homogenous air-hole structure on the butterfly wing. The photonic band gap could be tailored by adjusting the Ag adsorption time. Increase soaking time resulted in reflectance peak maximum shifting from 335-355 nm to 680-730 nm. Mu et al. utilized the chitin/chitosan found on butterfly wings for reduction to synthesize gold (Au) nanoparticles in-situ and presented its application as surface enhanced Raman spectroscopy (SERS) substrates.[108] The butterfly wing from *Morpho Menelaus* was about to detect 4-ATP at the

lowest concentration of 10^{-9} M and exhibit the lowest RSD among the others. Using the forewing of *Troides Helen* as a biomimetic template, Tian et al. modified the chitin forewing with amine moieties and subsequently deposited Au and CuS nanoparticles within the structure.[109] They later showcased its ability to improve infrared absorption, reduce reflectance, and capable of infrared (30.56 %) and solar photothermal conversion. Additionally, it achieved a solar absorptance up to 98 % when fabricated into a solar absorber. These features are associated with the plasmon-to-exciton/plasmon coupling effect between the nanoparticles together with favorable coupling between adjacent resonant systems in the sub-micrometer antireflection quasi-photonic structures of the forewing.

Chitin powder has also been explored as a starting material for photonic applications. A bio-ink derived from squid pen chitin functionalized with genetically produced amyloid proteins was developed by Wei et al..[110] The bio-ink was proven to be applicable for multiple fabrication techniques such as airbrushing, electrospinning, and lithography. Particularly, soft lithography was used to produce ordered and freestanding structures at micro-level. Potential photonic applications for fabricated structures as light guiding gratings include anti-reflection or photonic electrodes. To better understand the natural photonic observations, Liu et al. investigated the self-assembly of chitin nanocrystals within capillaries and found that the chitin nanocrystals form continuous orderly anisotropic phase dependent on phase boundary growth.[111] The air-liquid interface confined at the end of capillaries allows for concurrent evaporation and deposition of chitin nanocrystals which self-assemble into nested paraboloid Bouligand structures with density gradient. Continuous birefringent layers were observed as a result of directional evaporation. This study provided an insight into the biological self-assembly process of chitin nanocrystals found in living organisms.

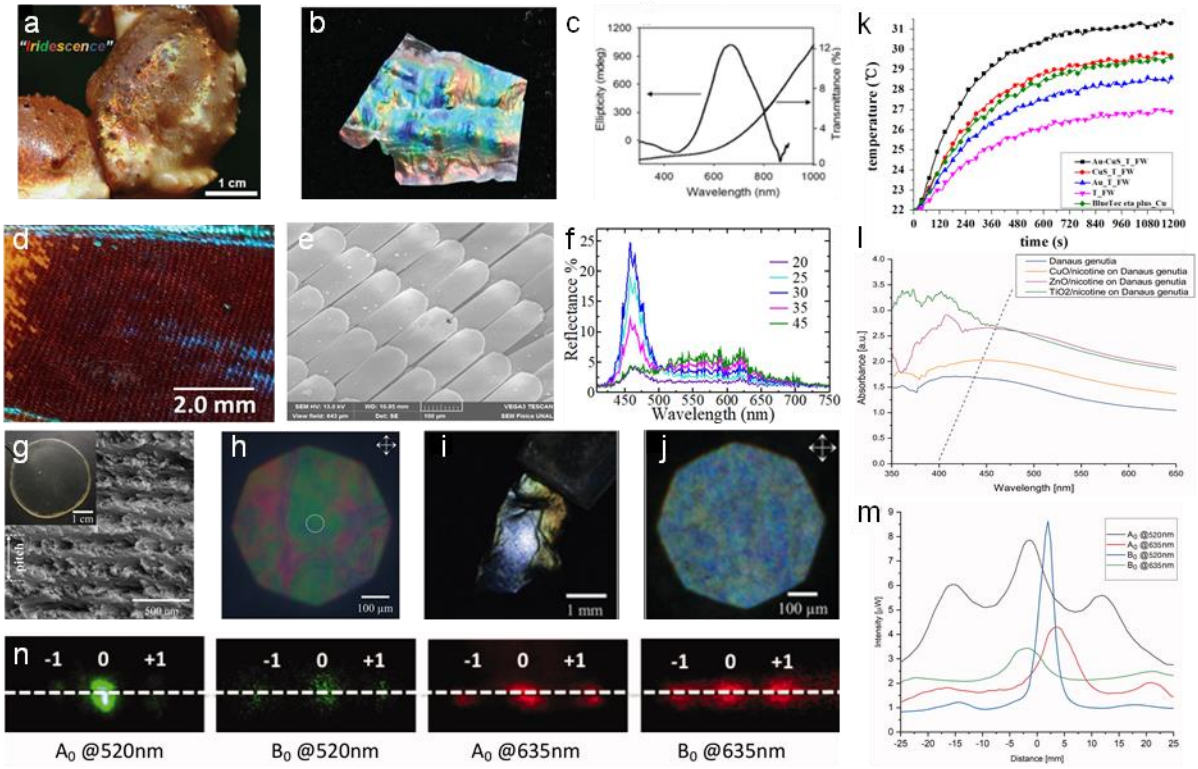

Fig. 8 Nanochitin for photonic applications (a) Optical image of a snow crab's claw displaying iridescence (b) Photograph of iridescent chitosan membrane derived from snow crab leg shells (c) UV-vis and CD spectra of chitosan membrane. Reproduced with permission.[112] Copyright 2019, John Wiley and Sons. Optical images of the *M. cypris* Colombian butterfly wing (d) 1x magnification, at 0° about the normal axis, viewed under the microscope (e) SEM image at the scale of 100 µm (f) Reflectance spectra of the *M. cypris* butterfly wing as a function of wavelength for the incidence angles of 20°, 25°, 30°, 35° and 45°. Reproduced with permission.[113] Copyright 2020, Springer Nature Limited. (g) SEM image of the cross-section of fungal chitin nanocrystal film (f-ChNC) and the film optical image was shown in the inset (h) Faint structural coloration observed for the f-ChNC film under the cross polarized microscopy (i) Image showing strong blue/green coloration of f-ChNC film flake after alkaline treatment (j) Microscopy image of f-ChNC film flake highlighting the blueshift of the reflected color. Reproduced with permission.[114] Copyright 2022, John Wiley and Sons. (k) *T. helena* forewings functioned as biomimetic template to produce photothermal conversion material

under the irradiation from a 980 nm laser. Reproduced with permission.[109] Copyright 2015, Elsevier Ltd. (l) The changes in the absorbance of the butterfly wing scales brought about by the deposition of the different metal oxide nanoparticles and nicotine mix (m) Distribution of the electric field intensity of the butterfly wing scales illuminated by red and green light (n) Far field diffraction of butterfly wing scales upon exposure to red and green light. Adapted with permission.[115] Copyright 2022, Informa UK Limited.

The challenge with fabrication of natural photonic structure arises from the difficulty to replicate the hierarchal structure without the use of a bio-template. Hence, many studies made use of the forewings of butterflies or other species which have photonic architectures as a native photonic template.[116-119] In addition, the stages of chitin biosynthesis that occur in living species require deeper understanding as it ultimately influences the final morphologies.

4.3 Nanochitin for Intelligent Food Packaging

Nanochitin in the form of nanofibers or nanocrystals have been well exploited as a reinforcing agent for traditional food packaging because of its non-toxicity and hydrophilic nature for the ease of dispersion in various aqueous polymer matrix.[120] It is also known to enhance physical properties (e.g., mechanical, thermal, barrier) of films. To advance traditional food packing for better monitoring and preservation of food, intelligent food packaging capable of providing cues on food freshness is desired. Anthocyanins are bioactive compounds that give rise to the different colors found in flowers, fruits, and vegetables.[121] Many have exploited natural anthocyanins extracted from various plants as the source of pH sensitive pigments. In general, anthocyanins are incorporated into a polymer matrix compatible for food packaging, entailing them with an intelligent feature to change color under different pH environment.[122]

Zheng et al. developed two colorimetric films for the evaluation of milk and pork freshness separately (**Fig 9a**).[123]The films consist of chitin whiskers filler, anthocyanins

extracted from black wolfberry, and sodium alginate or gelatin matrix. The films were able to exhibit visible color shifts between pH 3-12. The chitin whiskers were able to form hydrogen bonding and electrostatic interactions with the functional groups available in the other components resulting in reduced water solubility, improved thermal stability, and enhanced anthocyanin binding. Depending on its coloration response to extreme acid (e.g. lactic acid) or alkaline (e.g. ammonia) conditions, the films were concluded to be suited for detecting milk or pork spoilage. In another study, anthocyanin from red cabbage (RCAs) was added into a chitosan (CS)/oxidized-chitin nanocrystals (OCN) matrix by Chen et al.(**Fig. 9b and 9c**).[124] The RCAs were successfully integrated with CS/OCN via hydrogen bonding and color changing films were formed. The films exhibited visible color change according to the surrounding pH. When tested in the presence of hairtail (*Trichiurus lepturus*) and shrimp (*Penaeus vannamei*), color changed from reddish purple (fresh stage) to brown and lastly yellow (spoiled stage) was observed across 48 h. The color change strongly correlates with seafood spoilage process ($R^2 > 0.90$). Similarly, Sani et al. successfully entrapped red barberry anthocyanins (RBAs) into a composite chitin nanofiber (CNF) and methylcellulose (MC) matrix, thus forming a pH-sensitive colorimetric film.[125] pH-sensitive composite films were used to monitor the freshness of fish fillets over a period of 72 h. The decomposition process released volatile ammonia and amines which led to an increase in pH (6.3 to 8) and this is reflected by the colour change of the pH-sensitive film from reddish to pale pink.

Aside from anthocyanins, compounds such as curcumin which are pH sensitive can also provide observable colour indication for the monitoring of food spoilage. Curcumin (Cur) micro/nanoparticles were formed in-situ in a bacterial cellulose nanofiber (BCNF)/chitin nanofiber (CNF) composite film by Yang et al. (**Fig. 9d-f**).[126] With the incorporation of CNF, the Cur/BCNF/CNF film displayed improved mechanical and water barrier properties compared to Cur/BCNF film. This is due to CNF acting as a reinforcement nanofiller and a

hindrance to water diffusion. Colour change from yellow to reddish brown was observed when pH increased from 1 to 13 when Cur/BCNF/CNF films were immersed in solutions.

Another pH sensitive compound that was investigated was elderberry extract. Cabrera-Barjas et al. obtained nanofibrous β-chitin from squid pen waste and added glycerol alongside elderberry extract of varying concentration to form intelligent films for fish freshness monitoring.[127] Elderberry is considered a natural sensing pigment which displays different color in the presence of acid or alkaline surroundings. The films formed by combination of nanofibrous β-chitin and elderberry extract exhibited improved tensile strength and elongation at break. As the pH transited from 2 to 12, the film changed color from pink to grey. The combination of these properties makes the film suitable for food monitoring. They tested the film by monitoring the freshness of Hake fish and found that the film transited initially from pink to purple and subsequently, blue by day 6 due to the increasing basic environment caused by bacteria growth.

More recently, the incorporation of active ingredients to aid the preservation of food was explored by some. These additives provide additional properties such as antioxidant and/or anti-bacteria behaviors. Fernadez-Marin et al. investigated the addition of curcuma oil and anthocyanin extracted from *Curcuma Longa* L. and red cabbage respectively in a chitosan/chitin nanocrystal composite films.[128] Curcuma oil and anthocyanins were proven to be pH and ammonia sensitive components. The additional actives reduced moisture content and water solubility and increased ultraviolet light barrier and mechanical strength. Moreover, they endowed the film with antioxidant characteristics alongside color sensitivity to pH and ammonia variations. In another study by Duan et al., pullulan/chitin nanofibers were electrospun with curcumin and anthocyanins as active ingredients.[129] They successfully embedded curcumin and anthocyanins into the PCM substrate. The combination of both actives enhanced antioxidant and antimicrobial performance of the film compared to those that only

contained either. Films with anthocyanins were proven to exhibit distinct color changes when pH is varied. The PCN/CR/ATH nanofiber composite was tested by monitoring the decay of *Plectorhynchus cinctus* and observable color change was detected. Recently, natural red cabbage extracts (RCA) and nisin were immobilized into a chitin nanofiber reinforced pullulan/chitosan composite matrix by Wu et al..[130] RCA and nisin were well integrated and dispersed and formed hydrogen bonding with the other components within the composite. The inclusion of these active compounds also improved mechanical strength, thermal stability, water vapor and UV light barrier properties. The composite film exhibited antioxidant and antibacterial capabilities due to the presence of RCA and nisin respectively. Fresh food monitoring was demonstrated with sea bass (*Lateolabrax japonicas*) whereby the nanocomposite films changed from red (pH2) to blue (pH12) over the decay duration.

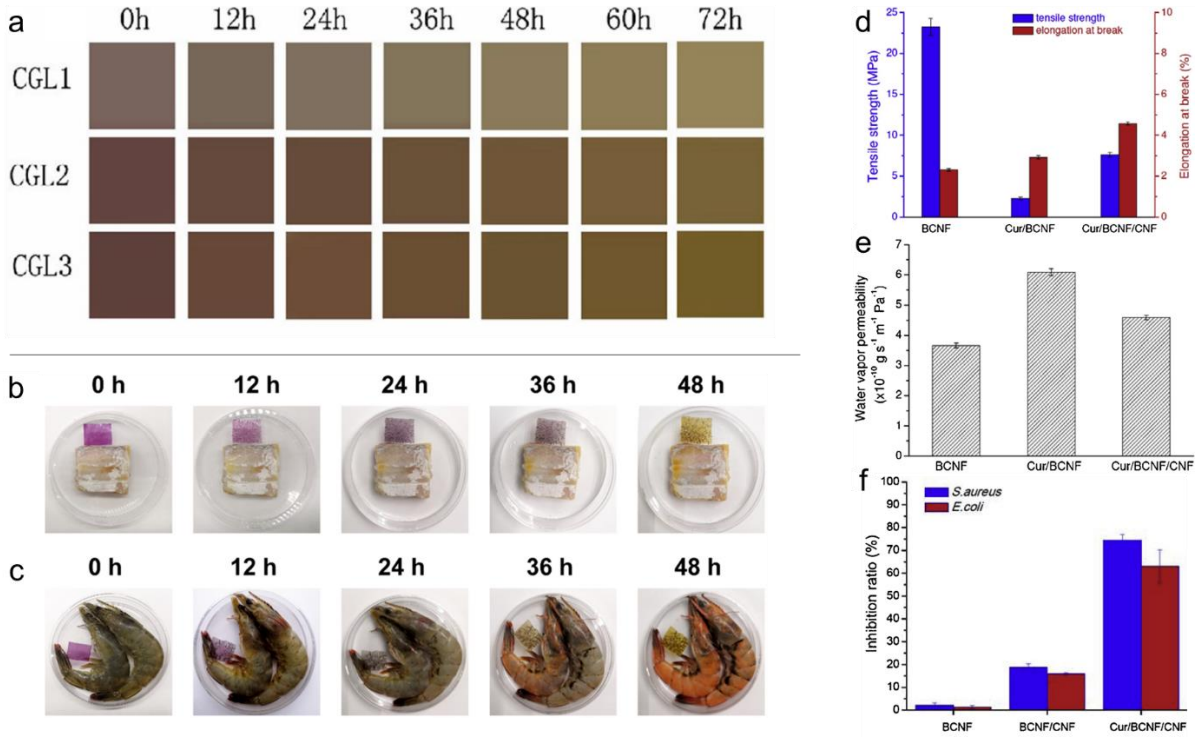

Fig. 9 Nanochitin for food packaging (a) Real time images of the color change displayed by the colorimetric films, developed with chitin whiskers, gelatin and anthocyanins, when stored with pork samples at 25°C for 72 hours. Reproduced with permission.[123] Copyright 2022,

Elsevier Ltd. Color indication captured by COR-1.2 films in response to the freshness of (b) hairtail and (c) shrimp during storage at 25 ˚C. Reproduced with permission.[124] Copyright 2021, Elsevier B.V. (d) Mechanical strength (e) Water vapor permeability (f) Inhibitory effects of the film samples against bacteria determined by CFU method. Reproduced with permission.[126] Copyright 2019, Elsevier Ltd.

In summary, nanochitin has been utilized as a reinforcing material to improve the natural limitations such as mechanical strength and barrier properties of polymeric films for food preservation. To provide a clear observable indication of food spoilage, plant-based athocyanins were exploited as pH-sensitive pigments for intelligent food packaging. Therefore, the combination of both chitin reinforcing agent and color changing pH-responsive extracts led to the development of smart films for food monitoring. These films can provide visual indication of food spoilage rate and at the same time have suitable physical properties for the preservation of food. To expand the capabilities of these nanocomposite films, additional active chemical compounds can also be incorporated to provide bioactivities which include antioxidant and antibacterial properties that aid with the preservation of food.

4.4 Nanochitin for Green Catalysis

Nanochitin is created by breaking down chitin into nanoscale particles using various physical and chemical processes.[1, 131-133] Thus, nanochitin possesses a high surface area, together with its biocompatibility, biodegradability and low toxicity, making it an attractive material for use in catalytic applications.[134-136] Due to the unique surface chemistry, nanochitin is an attractive material and has been intensively investigated for its potential use as a catalyst or as a support for catalytic materials.[137, 138] Nanochitin acts as the catalyst support for a wide range of catalysts, covering inorganic catalysts such as metal and metal oxides, as well as organic and biocatalyst such as organic molecules and enzymes.

4.4.1 Heterogeneous inorganic catalyst support

Heterogeneous catalysis systems are highly desired for the ease of catalyst/product separation, as well as catalyst recovery and recycling. One advantage of nanochitin as a supporting material is its biodegradability. Unlike conventional support materials such as carbon or silica, nanochitin can be easily degraded by natural processes, reducing the environmental impact of catalyst synthesis and use. On the other hand, the large surface to volume ratio of nanochitin allows for a high loading of metal nanoparticles and promotes efficient catalyst performance. The surface chemistry of nanochitin can also be modified to enhance its interaction with metal nanoparticles and improve catalyst stability. As displayed in **Table 3**, a summary of the common inorganic catalysts that nanochitin host in both catalytic chemical reactions and photocatalytic reaction systems.

Table 3: Summary of nanochitin supported inorganic catalyst systems.

Catalyst	Nanostructure	Reaction Scheme	Performance and Stability	Ref
Pd-chitin nanocrystals	Chitin nanocrystals	Heck coupling	• Yield 100%	139
Au-Chitin nanofibre membrane	Chitin nanofiber	4- nitrophenol Reduction	• As an indicator to show the successful recovery of Au NPs from Au^{3+} in the nanochitin matrix	140
	Chitin nanofiber	Peroxidase substrate 3,3,5,5 tetramethylbenzidine (TMB)	• Useful in the accurate and rapid determination of H_2O_2 • Potentially useful in food, pharmaceutical analysis	
	Chitin nanofiber	Glucose oxidation	• Oxidize the glucose while generate H_2O_2 • Important application for diagnosis of diabetes mellitus	
Pt-NP loaded macrofiber	Chitin nanofiber	Reduction of p-nitrophenol	• Achieved strain value of about 12% • Work-of-fracture is around 10 MJ/m^3. • Further loading with TiO_2 could enable photocatalytic property	141
Ag-NP/ Au-NP/Pt-NP nanochitin aerogel	Nanofiber	Reduction of p-nitrophenol removing of organic dyes	• Highly stable • The approach can be extended to other metal nanoparticle catalysts	142
ZnO/Chitin composite	Chitin/ZnO nanoparticle	Degrading NH4+–N under UV radiation	• 88.64% of NH^{4+}–N are removed in 2 hrs	143

			• To achieve catalyst cyclic utilization remains as unsolved problem	
Cu_2O-Chitin/Graphene oxide (GO)	Nanocomposite	Methyl orange (MO) degradation under sunlight	• Nanochitin act as template for Cu_2O nanoparticle synthesis • GO dramatically improve the photocatalytic performance of Cu_2O via enhanced charge separation • Great potential for waste water treatment using solar energy	144
Chitin-derived carbon/g-C_3N_4 heterojunction	Chitin-derived carbon nanoparticles	Rhodamine B degradation	• Non-metal photocatalyst which is cost-effective and sustainable comparing to metal based ones • Chitin create microstructural change for g-C_3N_4 leading to increment of surface area	145

Heterogeneous Support for Metal Nanoparticles

Nanochitin has several advantages as a support material for metal catalysts, including:

(i) With its high surface area, which provides more active sites for metal catalysts to be loaded onto and increases the accessibility of reactants to the catalyst.

(ii) Nanochitin is a biocompatible and biodegradable material, making it a sustainable and environmentally friendly alternative to synthetic support materials.

(iii) Nanochitin is highly chemically stable and can withstand harsh reaction conditions, making it a suitable support material for a wide range of metal catalysts.

(iv) Easy preparation: nanochitin can be easily prepared from natural chitin sources such as crustacean shells or fungal cell walls, making it a low-cost and readily available support material.

(v) Improved catalytic performance: nanochitin can improve the catalytic performance of metal catalysts due to its unique surface chemistry, which can enhance the adsorption of reactants and intermediates, and increase the selectivity of the reaction.

The metal catalyst nanochitin could support metal nanoparticles includes palladium, platinum, gold, and silver. Take palladium nanoparticles (Pd NPs) as an example, nanochitin-

supported Pd NPs have been used as catalysts for heck coupling reaction[139] and waste water treatment.[146] By directly reducing $PdCl_2$ salt in a one-pot fashion, Pd NPs are deposited onto the chitin nanocrystals and form the heterostructured catalysts.[139] From the Transmission Electron Microscopic images of the nanocomposites, one can see well-disperse Pd NPs on the surfaces of the nanochitin crystals. The authors took Heck coupling as a model reaction for testing the Pd NPs-chitin catalyst, obtained full product yield in mild conditions, outperforming the use of other biomass-supported catalysts, such as cellulose nanocrystals.

Another highly efficient metal nanoparticle catalyst is the platinum nanoparticles (Pt NPs), well known for its good catalytic performance in reactions such as hydrogenation, oxidation, and fuel cell reactions. Pt NPs exhibit high selectivity and stability even under harsh reaction conditions. Yet, the Pt NPs easily aggregate with the surface reactive site reduction when used alone. The nanochitin is on the other hand a great support substance for the Pt NPs during the catalyst fabrication. Das et al. developed a recycled nanochitin hydrogel loading with Pt NPs via in situ reduction of H_2PtCl_6 salt within the hydrogel matrix.[141] These organic/inorganic hybrid hydrogel fibers showed high activity in the catalytic reduction of p-nitrophenol at the presence of $NaBH_4$. Moreover, such recyclable catalyst systems can be developed further with the addition of TiO_2 nanoparticles and perform photocatalytic reactions.

Silver nanoparticles (Ag NPs) is another multifunction nanoparticles which is widely utilized in antibacterial coatings, sensors, water treatments, solar devices and catalytical reactions. As shown in **Fig. 10a**, with the dopamine activated nanochitin gel-like matrix, Ag+ ions are introduced and further reduced into Ag NPs, followed by freeze drying to obtain the aerogel of hybrid Ag-nanochitin.[142] By controlling the activation of the nanochitin matrix via dopamine, the author could control the storage capacity and the size distribution of metal nanoparticles precisely. With high surface area, low density, tough mechanical strength and excellent catalytic activity, the hybrid aerogel reduced organic pollutants (such as methyl

orange, methylene blue, p-nitrophenol and rhodamine B) in $NaBH_4$ medium, examples are displayed in **Fig. 10b** and **10c** respectively. This approach could be used for generating many other catalytic metal nanoparticles with nanochitin aerogel, such as Au and Pt as demonstrated by the authors of the work.

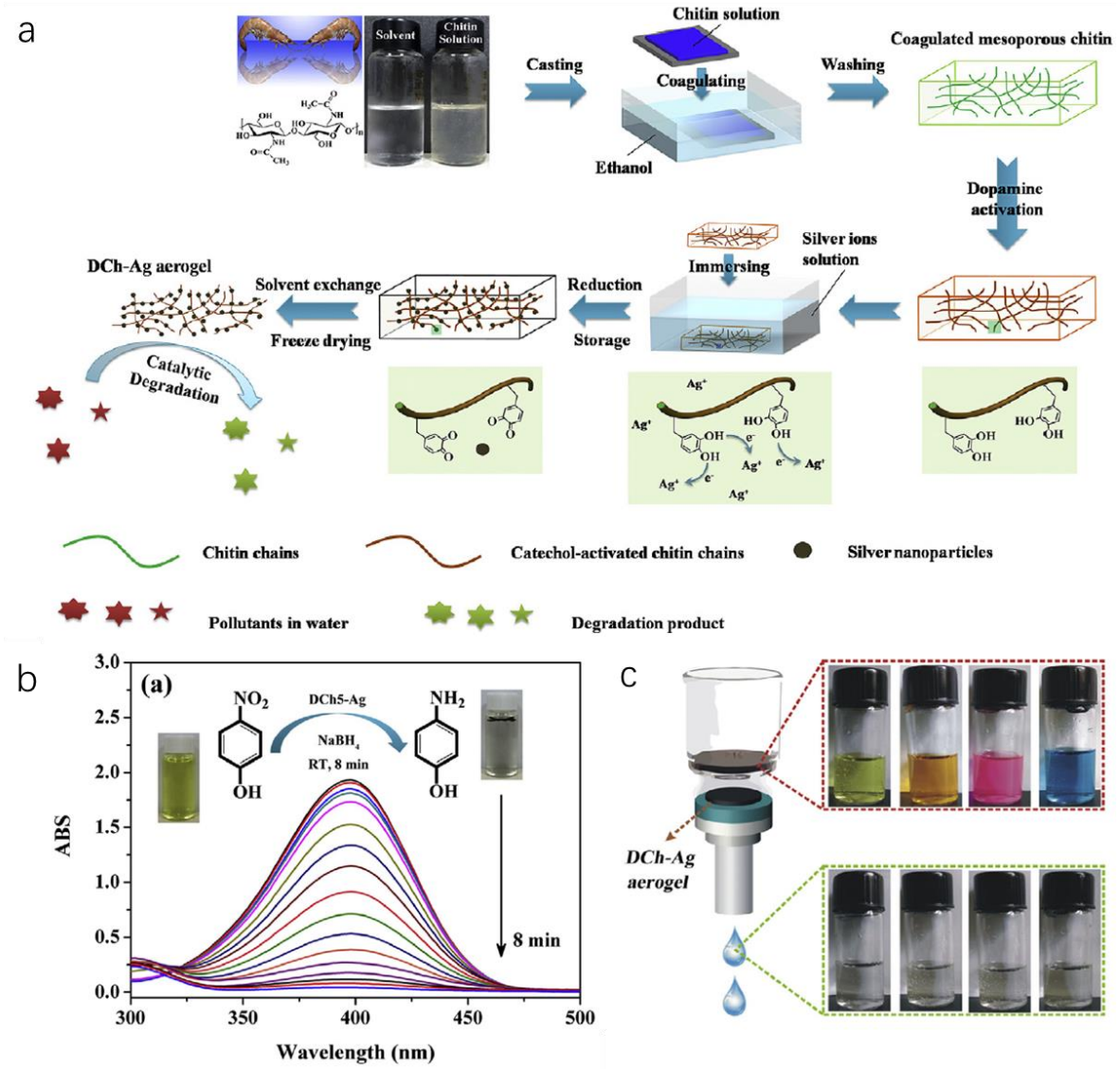

Fig. 10 (a) Illustration of fabrication of the ChNC-Ag aerogel. (b) Catalytic evaluation of ChNC-Ag NPs aerogels with a typical UV–vis spectra of the conversion reaction. The inset photographs show the color change from yellow (before) to colorless (after). (c) ChNC-Ag aerogels as filtration membranes to remove organic pollutants, four colored organic dyes turn to colorless after filtration process. Reproduced with permission.[142] Copyright 2017, Elsevier Inc.

Last but not least, nanochitin can be chemically modified, for example introducing amino groups, the chitin nanofibers that are used in filtration membranes allowing effective extraction of noble metal ions, such as Au^{3+}, Ag^{+}, Pt^{4+}, and Pd^{2+} [140]. As shown in the schematic drawing in **Fig. 11a**, firstly the nanochitin fiber membranes absorb metal ions from the oil/water emulsion, then with an in-situ reduction of the absorbed metal ions, metal nanoparticle loaded nanochitin fibers were obtained.[140] Such nanochitin supported metal catalyst would be then potentially useful for catalytic applications for the purpose of biosensing and green catalyst production. Here in this work, Au^{3+} was introduced to demonstrate the excellent catalytic property of the recovered Au NPs-nanochitin fibers in the membrane form. The actual color of the recovered nanochitin membrane turns from yellow to red, along with TEM results, demonstrate good size and crystallinity of the Au NPs. Two model reactions were chosen to test the Au NPs-nanochitin fiber catalyst with the results displayed in **Fig. 11b** and **11c** respectively. With the same approach, Ag, Pt and Pd nanoparticles could also be obtained for the metal nanoparticle-nanochitin fibers catalyst, though the authors didn't report such experiment. The successful recovery of Au NPs-chitin fibers membrane demonstrates great catalytic activities and potential uses in sensor and green catalysis systems.

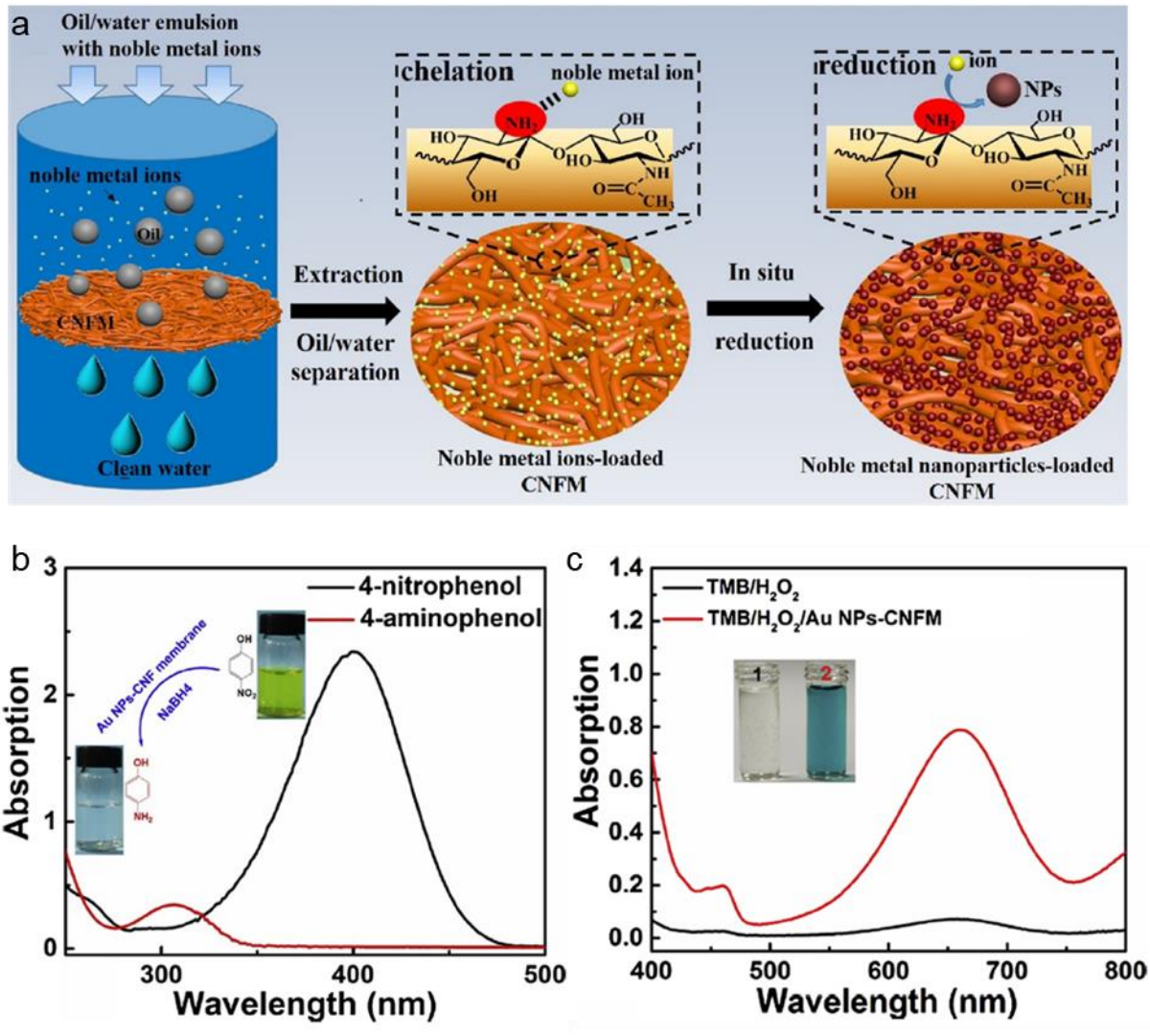

Fig. 11 (a) Scheme illustration of the recovery of noble metal ions from oil/water emulsions by chitin fibres membranes. (b) UV-vis of the 4-nitrophenolate/NaBH4 before and after treated by Au NPs-nanochitin fibres. (c) UV–vis spectra of TMB/H_2O_2 before and after treated by Au NPs- nanochitin fibres. The insets are the photographs of TMB/H_2O_2 before (1) and after (2) treated by Au NPs- nanochitin fibres. Reproduced with permission.[140] Copyright 2019, Elsevier Ltd.

Support or Additive for Inorganic Photocatalysts

Metal oxide and other inorganic nanoparticles, such as titanium dioxide (TiO_2)[147, 148], zinc oxide (ZnO)[143, 149], copper oxides (Cu_2O)[144] and carbon nitride (C_3N_4)[145] can be deposited onto the surface of nanochitin and used as a catalyst for various reactions. The biodegradability of nanochitin is advantageous, as it reduces the environmental impact of catalyst synthesis and

use. Some of the reported works are included in **Table 3** for these materials demonstrating attractive properties and good photocatalytic behaviour.

Instead of depositing onto the nanochitin surface, Nguyen et al. utilized a different strategy known as liquid crystal self-assembly to develop TiO_2/graphene/chitin composite membranes.[150] Liquid crystals of both graphene oxide nanosheets and chitin nanospindles supposedly self-assembled into a flexible nacre-mimicking membrane and peroxotitanate was incorporated into the structure during the co-assembly process. A subsequent reduction was performed to produce TiO_2/graphene/chitin composite membranes. The absorption ability of this composite membrane was revealed to be much enhanced as compared to the graphene oxide (~235 nm). In fact, the absorption range of the composite membrane was found to have extended to the visible light band (~450 nm). Additionally, they showed that the developed membrane could photocatalyze methylene blue solution to colorless within 30 minutes of UV-Vis irradiation which was faster than the controls (graphene and Degussa P25). This was attributed to the synergistic semiconductor-graphene interactions which was made possible by the heterojunction of the TiO2 nanoparticles-localized graphene nanosheets supported onto the nanochitin layers.As the surface chemistry of nanochitin can be modified to enhance its interaction with inorganic nanoparticles, together with the template effect that facilitates synthesis and distribution of the catalyst, nanochitin is an effective component that can improve the catalytic performance from several aspects.

4.4.2 Biocatalyst Support

Biocatalysts are enzymes or microorganisms that can catalyze chemical reactions, and they have a wide range of industrial and biomedical applications. Nanochitin has been used as a natural polymer support for various biocatalysts, including enzymes and whole cells.[151, 152] The biodegradability of nanochitin is advantageous in biocatalytic applications as it reduces the need for costly and environmentally harmful support material disposal. Additionally, the

unique surface chemistry of nanochitin can be modified to enhance the interaction between the support material and biocatalysts, promoting improved biocatalyst stability and activity. There are many biocatalysts reported in the field, including lipase[153, 154], glucose oxidase mainly for biosensors[155], and horseradish peroxidase[156]. The choice of immobilization method depends on the specific enzyme, chosen supporting materials and the intended application. Examples of the explored immobilization methods include but not limited to physical adsorption, ionic binding and covalent binding.[157] Take enzymatic esterification reaction as one of the actual applications of the lipase, a biocatalyst is developed via chitosan-chitin nanowhiskers supported Rhizomucor miehei lipase.[158] With optimized conditions, the authors reported a maximum yield of 66% at 50 °C in 5 hours reaction. The immobilized lipase as an efficient biocatalyst could be used for up to 8 cycles of esterification without degradation.

Nanochitin serves as immobilization support for enzymes and other biocatalyst and are very useful in industrial biotechnology such as the production of pharmaceuticals, food processing, and biofuels. In general, the immobilization of enzymes on nanochitin can improve their stability, activity, and reusability, leading to more efficient and cost-effective enzyme-catalyzed processes.

4.4.3 Organocatalyst

Organocatalysis is a type of catalysis that involves the use of organic molecules as catalysts to promote chemical reactions. Nanochitin has been shown to have catalytic activity in various organic reactions, such as the Michael addition, the aldol reaction, the hydrolysis of cellulose and the synthesis of organic carbonates. As a biopolymer organocatalyst, nanochitin is more advantageous than the traditional organic molecules:

(i) The high surface area of nanochitin allows for a greater number of active sites, leading to higher catalytic activity;

(ii) The biocompatibility of nanochitin also makes it a more sustainable and environmentally friendly alternative to synthetic organic catalysts.

(iii) With amino and carboxyl functional groups that participate in the reaction mechanism, nanochitin can be more selective and achieve higher catalytic efficiency.

Tsutsumi et al. reported highly porous nanochitin aerogel with C2-amine functionalized chitin nanofibrils (ChNF), exhibiting high surface areas.[159] The obtained nanochitin aerogel served as the catalyst for the aqueous Knoevenagel condensation reaction, achieved high efficiency due to the combination of active amine groups and the nanofibrous structure supporting continuous flow catalysis. Amino-functionalized nanochitin and chitosan has been shown to be an effective catalyst for solvent-free synthesis of chalcones[160], self-condensation of linear aldehydes[161] and Biodiesel Production[162]. Nanochitin can also be used as bioreactors for various purposes, such as sulfate reducing for mining influenced water[163], metal removal and acid neutralization[164], as well as creating multienzyme bioreactor[165]. The high surface area of nanochitin allows for efficient cell attachment and growth, and the unique surface chemistry can be modified to enhance the interaction between cells and the supporting material.

Although nanochitin has great potential for use in catalytic applications due to its unique properties and versatility, further research is needed to fully understand its catalytic activity and to optimize its use in different applications.

In summary, using natural polysaccharides such as chitin as either catalyst support or organocatalyst itself, is an emerging trend in green and sustainable chemistry. There are much exciting scope remains unexplored in utilizing natural polymers in sustainable chemistry. For instance, it can be explored as catalyst for oxygen evolution reaction[166, 167] or high kinetics oxygen reduction reaction[168].

5 Conclusion and Perspective

In this review, we have summarized the different strategies to prepare nanochitin from chitin. We examined these strategies from a different angle by identifying the comparably more sustainable methods from the traditional methods. For instance, researchers have explored the use of greener solvents and ways to optimize the process to be more environmentally friendly. It is recognized that chitin sources can be obtained from various biomass such as crustaceans, insects, and fungi. The efficiency of chitin isolation from these sources is different even when the same technique is used due to the different compositions that it is found in. For example, chitin extraction from insect exoskeleton is likely to be easier than chitin isolation from crustacean shells where the mineral content is higher. Not only can milder conditions be used for the former, but the yield can also be higher.

At present, the chitin biorefinery is not as established as its cellulose counterpart. Referencing to the market size of the nanocellulose, it can be safely estimated that there will be a market for the nanochitin. In fact, the market size of the nanochitin will not be small and likely to be even bigger than the nanocellulose. The reason being that nanochitin is the only natural polysaccharide that contains nitrogen. While the actual extent of demand for the nanochitin and its products is still unclear, all above studies have demonstrated that nanochitin will be valuable as a sustainable and advanced materials for future manufacturing, consumer care and even biomedical fields.

It seems that several challenges need to be overcome in the process of establishing the chitin biorefinery. The first challenge is to isolate and obtain homogeneous sources of biomass waste. There is also the problem with resource complexity whereby different sources have different chitin contents. The nanochitin extraction methods are currently still not very eco-friendly with low yield despite being energy intensive. The characterization, processing and modification methods are very limited at this stage. At present, nanochitin is mostly applied as an additive instead of bulk materials and more studies will be needed to understand its

interaction with the host matrix. There is also the question of the feasibility of scale up, which should be possible given its predecessor – nanocellulose. However, the success of scale up eventually depends on the techniques employed to extract chitin and convert it to nanochitin as well as the efficiency. A crucial and unavoidable issue would be the cost of the nanochitin fabrication as a high cost will deter its use for applications.

Besides the challenges encountered in the set-up of chitin biorefinery, it is necessary to consider the environmental impact of the nanochitin fabrication from cradle to grave. It is important to reduce and valorize waste, however, there should not be more waste generated in the process of doing so. Life cycle assessments would be a powerful tool to gauge the "real" environmental benefits of the nanochitin synthesis from biomass waste.

Finally, potential applications for nanochitin in advanced manufacturing that have been explored by researchers are presented which range from 3D printing, photonic to packaging and catalysis. Indeed, nanochitin appears to have numerous advantages that can be imparted to the materials. However, in most cases nanochitin can only be used as additives or supportive materials. How to better explore its advantage and maximize its potential is something worthy to investigate, to achieve a circular economy.

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Conflict of Interest

The authors declare no conflict of interest.

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