



## Feature Article

## Different routes to turn chitin into stunning nano-objects



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## ABSTRACT

Due to its intractable structure and inherent insoluble nature, chitin was for a long time an underutilized resource. The increasing interest in the use of chitin as a source of nanostructured materials is quite recent. This review provides the latest advances in different ways to isolate or fabricate chitin nano-objects – chitin nanocrystals (CHNC) and chitin nanofibers (CHNF) – from different chitin sources. It also summarizes the chronology of some important scientific advances on chitin research during its 200 years of history. Additionally, engineered composite materials based on chitin nano-objects are reviewed.

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## 1. Introduction

In 1811, the French botanist H. Braconnot isolated from mushrooms a polysaccharide of major importance: *chitin* (by this time identified as *Fungine*) [1,2]. A point of difference from other polysaccharides is the presence of nitrogen. Years later, in 1823, another French scientist, A. Odier identified chitin in demineralised crab carapace and suggested that it is the basic material of the exoskeleton of all insects. The term chitin is derived from the Greek word  $\chi\iota\tau\omicron\nu\nu$ , which means ‘tunic’ or ‘covering’ [1]. In fact, chitin is biosynthesized by a vast number of living organisms. It is commonly found in the crustacean shells, insect cuticles and in the cell walls of fungi, yeast and green algae [1,3,4]. Chitin is a crystalline high-molecular-weight linear polymer composed of *N*-acetyl-2-amido-2-deoxy- $\beta$ -D-glucose units linked by  $\beta(1 \rightarrow 4)$  bonds (Fig. 1). Isolated chitin is a highly ordered copolymer of *N*-acetyl-D-glucosamine as the major component and D-glucosamine as a minor constituent (Fig. 1). These residual monomers are present in the native chitin or are formed through hydrolysis of some acetamido groups during the isolation and purification processes [1].

Chitin was for a long time considered as an untreatable polymer because of its inherent insoluble nature (in almost all common solvents) and intractable molecular structure [4–6]. In 1920s and 1930s numerous methods were developed to obtain chitin fibers for the production of artificial silk. However, the interest in chitin decreased quickly with the discovery of nylon and production of synthetic fibers [7].

Only in the late 1970s did chemists look at chitin with scientific interest, and immediately recognized it as an abundant source of chitosan – the unique cationic polysaccharide [1,6]. Chitosan, the major and simplest chitin derivative, is also a high-molecular-weight linear polymer obtained by deacetylation of chitin (cleavage of the *N*-acetyl group at C-2 position) and is therefore composed of 2-amino-2-deoxy- $\beta$ -D-glucose units linked through  $\beta(1 \rightarrow 4)$  bonds (Fig. 1) [1,3,4,8–10].

Nonetheless, the increasing interest in the use of chitin and chitosan in several applications only started at the beginning of the 1980s because of environmental requirements due to the organic solid wastes and by-products generated by the food industry (in particular, shellfish

industries and fish farms in Japan and USA). Part of the massive amount of biowaste accumulated (up to 250 billion tons/year) by marine-capture fisheries can be industrially transformed in pure chitin and its derivatives. It is estimated that at least 10 gigatons of chitin is biosynthesized and degraded each year – chitin is considered to be the second most abundant biopolymer on earth after cellulose [8,9].

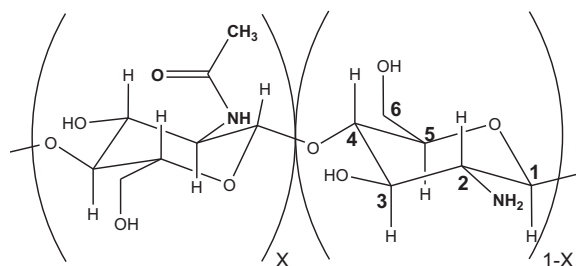
Despite being one of the most available natural polymers, chitin was for a long time an underutilized resource, when compared to the other polysaccharides (including chitosan), due to its insoluble character. It is a quite recent trend that pristine chitin has gained importance as a promising source of new materials – as a nanostructured material in the form of chitin whiskers and/or nanocrystals (CHNC) and chitin nanofibers (CHNF) (altogether called here as chitin nano-objects). One of the first works describing the use of chitin whiskers as new environmentally friendly reinforcing agents in thermoplastic nanocomposites was reported in 2001 by Paillet and Dufresne [11]. Following, new domains of exploitation of chitin have emerged for using it over a broad range of applications including nanocomposite materials, electronics and medical devices and cosmetics [12–16].

Unquestionably, the key consideration of the growing scientific interest in chitin nano-objects is the atypical combination of physicochemical and mechanical properties as well as biological properties. Chitin is widely abundant, biodegradable and biocompatible with low cytotoxicity, present antimicrobial activity and low immunogenicity. Moreover, chitin nano-objects have high aspect ratio, high surface area, low density and reactive surface ( $-\text{OH}$  and  $-\text{NHCCH}_3$  groups, and residual  $-\text{NH}_2$  groups) that facilitates surface functionalization [3,4,8,9,12,13,17–19].

In this context, recently several methods have been developed to isolate chitin nano-objects from chitin source materials [11,14,20–32]. This review describes and discusses the advances on the research work on different routes to turn chitin in stunning nano-objects.

## 2. Supporting material in living systems

Why can chitin be turned into nano-objects? In nature, chitin occurs as a highly-organized micro- and nano-fibril structure, whose role is that of providing support and protection to living systems, mainly to crustaceans, insects and fungi, as reinforcing and functional elements [10,12,14,33–35]. Chitin forms part of a well organized hierarchical structure (Fig. 2), in the exoskeleton of many invertebrates – such as crabs, shrimps, lobsters and krills – increasing from the nanometer to the millimeter scale. As shown in Fig. 2, at the molecular level, there are long chains of chitin that form highly crystalline fibrils on the nanometer level (length ( $L$ )  $\sim 30$  nm, width ( $d$ )  $\sim 3$  nm). Within these fibrils, chitin chains are packed together forming highly crystalline regions that are accompanied by disordered (amorphous) regions, making chitin semicrystalline. These fibrils are enveloped with proteins and assemble into nanofibers ( $d \sim 60$  nm), which further



**Fig. 1.** Illustration of the chemical structure of copolymers chitin ( $X \gg 1 - X$ ) and chitosan ( $1 - X \gg X$ ) of *N*-acetyl-D-glucosamine (molar fraction =  $X$ ) and D-glucosamine units (molar fraction =  $1 - X$ ). Conventionally, chitin  $X > 0.50$  and chitosan  $X < 0.50$ .

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