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# Biogenic nanomaterials from photosynthetic microorganisms

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The use of algal cell cultures represents a sustainable and environmentally friendly platform for the biogenic production of nanobiomaterials and biocatalysts. For example, advances in the production of biogeneic nanomaterials from algal cell cultures, such as crystalline β-chitin nanofibrils and gold and silver nanoparticles, could enable the 'green' production of biomaterials such as tissue-engineering scaffolds or drug carriers, supercapacitors and optoelectric materials. The *in vivo* functionalization, as well as newly demonstrated methods of production and modification, of biogenic diatom biosilica have led to the development of organic–inorganic hybrid catalytic systems as well as new biomaterials for drug delivery, biosensors and heavy-metal adsorbents.

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## Introduction

Algal cell cultures are promising systems for the 'green' synthesis of nanomaterials, such as nanostructured and nanocrystalline biopolymers, metallic nanoparticles (NP) and hierarchically structured nanomaterials, as well as for the *in vivo* functionalization of biomaterials and entrapment of enzymes. This review will summarize the latest developments, applications and production methods of these materials from algal-based systems. Recent works and reviews have described the potential device applications of nanostructured materials from the silica-based cell walls, or the polymer and metallic replicas of these structures, from marine and freshwater diatoms. Such applications include optoelectronic devices, solar cells, gas sensors, and battery electrodes [1–4]. Another recent review by Galloway *et al.* [5] describes the synthesis of nanomaterials based on various living systems, such as butterflies and viruses, as well as some photosynthetic systems. In addition to the most recent advances within the previously mentioned applications, this survey will focus on the latest progress using strictly biologically produced algal-based nanobiomaterials, rather than biomimetic, bioclastic or biokleptic materials, in emerging fields such as the production and application of nanocrystalline biopolymers, synthesis of metallic NP and the *in vivo* fabrication of hybrid organic–inorganic materials. This work will also address new insights into the micro-scale and nano-scale biosilicification process derived from newly developed numerical models.

## Nanostructured biopolymers

### Crystalline β-chitin nanofibrils

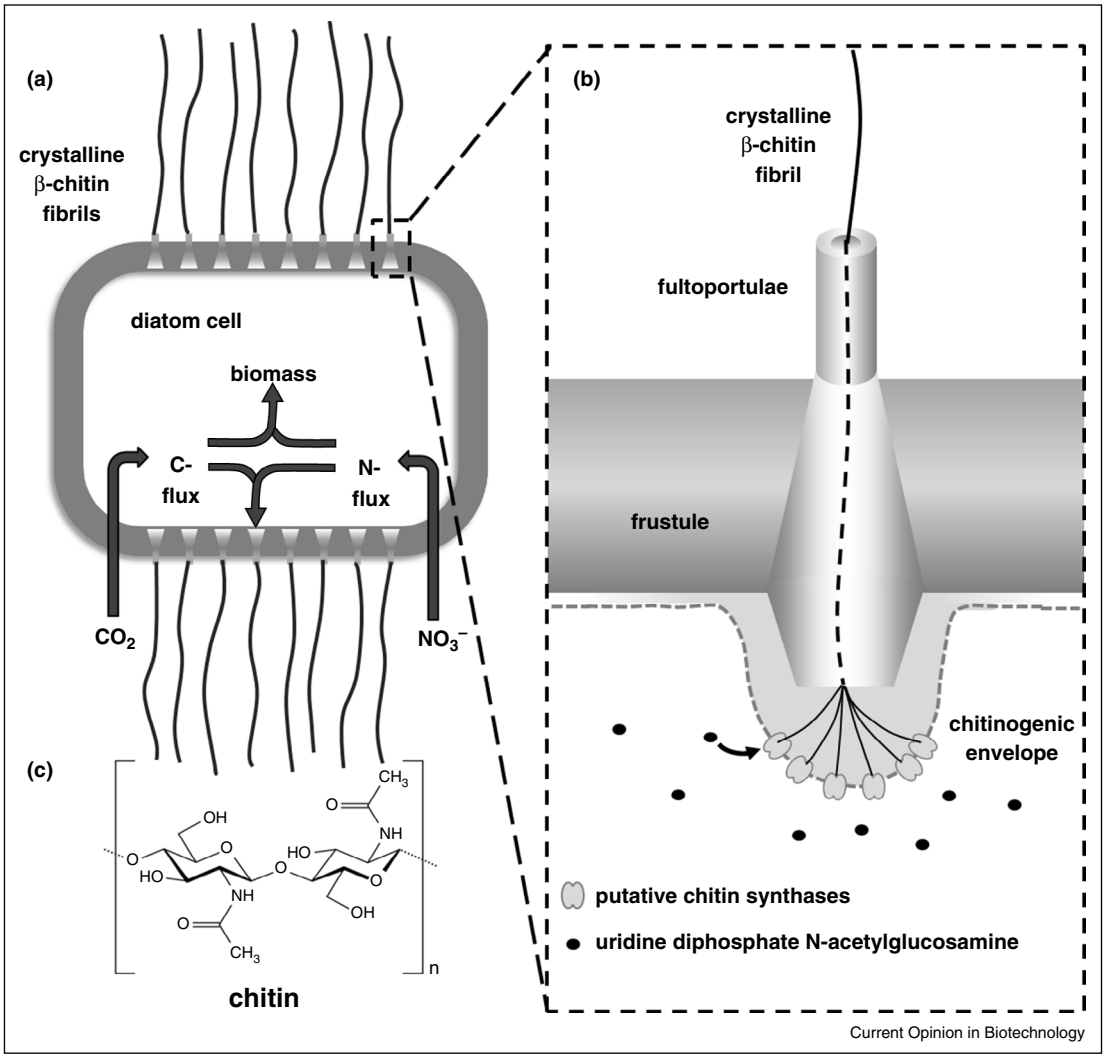
Chitin nanofibrils are biopolymers with a high degree of thermal and chemical stability and mechanical strength. These polymers have demonstrated wound-healing properties, such as the promotion of cell migration and proliferation as well as anti-microbial activity [6], and have also been used as scaffolds for tissue engineering [7], neural network templating [8] or in supercapacitor electrode materials [9].

Chitin nanofibrils are known to be produced by stationary phase cultures from the diatom genera *Cyclotella* and *Thalassiosira* with the latter known to excrete long aspect ratio (tens of microns in length, ~30 nm diameter) fibrils which are highly crystalline without the need for post-processing or harsh chemicals [10]. The chitin fibril extrusion process in diatoms, adapted from [11], is presented in Figure 1. Crystalline β-chitin fibrils from *Thalassiosira weissflogii* have recently been used to template nanostructured organic–inorganic silica hybrid materials [12], as well as to form nanostructured crystals with heavy metal cations such as $Pb^{+}$, $Gd^{3+}$ and $UO^{2+}$ [13] and as a material to facilitate the aggregation of human pathogens [14•,15]. Nanocrystalline chitin fibrils have also been used to template nitrogen-doped carbon materials in supercapacitor electrodes [9]. A similar aspect ratio, cellulose-like nanofibril material was made from a β-1,3-glucan biopolymer produced by cell cultures of *Euglena gracilis* [16]. This material was mechanically strong, biodegradable and produced by a bottom-up approach which avoided mechanical or enzymatic treatments.

## Production of gold and silver NP

Conventional formation of zero-valence NP, such as $Au^{0}$ and $Ag^{0}$, is achieved by methods such as lithography, laser

**Figure 1**




The production of crystalline β-chitin fibrils from diatom cell culture. **(a)** Under silicon starvation the cell continues to take up $CO_2$ and $NO_3^-$. The C-flux and N-flux are directed towards biomass and extruded chitin fibrils. **(b)** Putative enzymes in the chitinogenic envelope polymerize monomer units of uridine diphosphate N-acetylglucosamine to form the chitin strands which align to form the chitin fibril. The fibril is then extruded through the fultoportulae and into the extracellular environment (adapted from [11]). **(c)** The chitin repeat unit.

ablation or gas phase aerosol generation, which remain expensive and use harmful chemicals. However, the scalable, 'green' synthesis of NP from cell cultures can be accomplished at ambient temperatures and pressures in simple cell culture media [17]. These NP are known to have antibacterial properties and have applications in drug delivery, catalysis and optics [18].

Numerous *in vivo* mechanisms for the uptake and reduction of $Ag^+$ and $Au^{3+}$, respectively, to $Ag^0$ and $Au^0$ NP have been proposed in the literature. These processes, adapted from [19•,20,21], are presented in Figure 2. For example, the uptake of metal cations can be brought about by an osmotic process [20,22] or mediated by transmembrane proteins such as Cu(I) ATPase [21], but the mechanism of reduction and the type of NP produced are species dependent. The reduction mechanism of $Au^{3+}$ to $Au^0$ could result from electron transfer from carboxyl groups, polyphosphates or polysaccharides on the surface of the cell wall or organelles [23], or from reduction by electrons or electron mediators generated by the algal cell's photosystem (e.g. within the $NADP^+$/NADPH redox cycle, recycled via energy generating reactions in the photosynthetic electron transport chain) [19•,20,23]. When cell cultures of *Tetraselmis kochinensis* were exposed to $HAuCl_4$, the result was 5–35 nm $Au^0$ NP which remained bound to the cell wall and cytoplasmic membrane [24]. However, when