Liquid crystal templating of nanomaterials with nature's toolbox

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ABSTRACT

Naturally occurring biomolecules are sustainable and green precursors for the development of new materials. Within this family of natural materials, cellulose nanocrystals (CNCs) have emerged as one of the most promising materials because of their outstanding physico-chemical properties and the possibility to produce them in large quantities. One key trait of CNCs is their ability to self-assemble into a chiral nematic liquid crystalline phase. In this review, we discuss how templating can be used to transfer the three-dimensional structure of liquid crystalline CNC phases onto solid materials. This is followed by examples that illustrate the fascinating properties and potential applications that arise from the resulting nanostructured materials such as sensing and catalysis. We then summarize efforts to use the liquid crystalline phase of a selection of other biopolymers for templating. While nanocrystalline chitin, having very similar properties to CNCs, has been successfully employed to make a variety of new materials, efforts to template liquid crystal phases of other biomolecules have been met with limited success. However, we discuss virus nanoparticles and collagen as examples to highlight further possibilities for materials research.

1. Introduction

Nanoscience and nanotechnology have the potential to revolutionize health care, transportation, food, and other massive areas of our lives [1]. With features that are only 1–100 nm in length – a mere fraction of the width of a hair – nanostructures and nanomaterials are being incorporated into sensors [2,3], solar cells [4,5], displays [6,7], batteries [8–10], and many other technologies. Much of the recent developments in the field have been driven by the development of instrumentation that allows for rapid visualization and manipulation of features on this length scale, allowing one to rapidly screen and evaluate new synthetic materials. Indeed, the synthesis of nanostructured materials is of paramount importance for developing new nanotechnologies. Chemists have many methods at their disposal to control the composition, structure, surface chemistry, and hierarchical organization of nanomaterials. Top-down approaches such as ball milling and etching allow one to transform a bulk material into a nanostructured form. On the other hand, bottom-up approaches, such as self-assembly, are emerging as powerful means to develop new structures with controlled architectures and narrow size distributions [11].

Porous materials with nanometer-scale holes are attractive for separation membranes [12], gas storage [13,14], catalyst supports [12,15,16], and other applications. There have been tremendous efforts expended to develop porous materials with control over pore sizes, shape, and arrangement. In the case of zeolites, it is a cation that functions as a template for the formation of a porous, ion-exchangeable aluminosilicate framework. By changing the size of the cationic template, it is possible to control the size of the channels in the structure. Small molecular templates are an excellent route to porous materials with pores up to ~2 nm in diameter, but accessing materials with larger pores requires a supramolecular approach where the template is something larger than a molecule or small ion.

In 1992, Kresge et al. reported a breakthrough in the field of materials chemistry, now known as liquid crystal templating [17,18]. By condensing tetraethoxysilane (TEOS) in the presence of a surfactant, they obtained amorphous silica with a hexagonal honeycomb lattice of holes filled with surfactant. Upon removal of the surfactant, the resulting mesoporous materials (called MCM-41) contained a periodic arrangement of pores with diameters that could be adjusted from 1.5 to ca. 10 nm. The materials are thought to be formed by templating, where silica is condensed in the aqueous regions around a pre-assembled liquid crystalline phase of the surfactant. (Note that this mechanism is widely accepted but not fully supported in the case of MCM-41 [19]). Using surfactants with chiral head groups gives mesoporous materials with twisting channel structures [20].

Since the discovery of MCM-41, a variety of liquid crystalline templates have been employed to make porous materials. Diverse molecular and polymeric, ionic and neutral substances have been used as templates. Templating has been performed in water, alcohol, formamide, ammonia, and other solvents. Block copolymers (e.g. Pluronics), in particular, can be used to template porous materials with much larger holes than molecular surfactants [21,22]. As well, the symmetry of the

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pores and their connectivity can be controlled by choosing appropriate templates.

Despite the significant advances in templating with synthetic molecular and polymeric substances, these templates are very simple compared to the vast, complex templates available in nature, such as proteins, carbohydrates, bone, and DNA. Nature's templates have complexity both at the molecular scale and in their supramolecular organization [23], all of which may be imprintable in a nanostructured material. Conceptually, the materials and structures found in nature offer a rich and sophisticated toolbox of templates that can be used to make complex materials with hierarchical structures. As well, these materials are biodegradable and often renewable. One recent example where natural materials were directly employed as a template is the deposition of silsesquioxanes on the chitin skeleton of a marine sponge [24].

Many natural substances, such as DNA, cellulose, and silk are known to form liquid crystals in water or other solvents [25–29**]. In these structures, the biomolecules are organized into chiral hierarchical assemblies that span multiple length scales. These assemblies present exciting opportunities for templating, and chemists are now widely exploring these substances as templates [30]. Here, we take you on a journey through the various classes of liquid crystalline biomolecules that have been applied as templates to construct porous materials. Although this review is not comprehensive, it is our goal to capture the excitement in the area with a focus on cellulose nanocrystals (CNCs) and nanocrystalline chitin (NCh).

2. CNCs

2.1. Properties

Cellulose is one of the most abundant and versatile biopolymers found in nature. It is commonly isolated from the cell walls of plants and algae but can also be isolated from certain species of bacteria, fungi and marine animals [31,32]. Cellulosic materials are widely used in the pulp and paper industry but are also being investigated as additives in composite materials, in medical applications and as a templates [33–35**]. Its unique combination of mechanical support, flexibility, abundance and biocompatibility presents promising applications for cellulose in the field of materials chemistry.

Naturally derived cellulose microfibers are isolated from the cellular matrix through either alkali or oxidative extraction treatment, usually 2–4% NaOH at elevated temperatures, or acidic treatments followed by subsequent bleaching to remove soluble polysaccharides and residual phenolic molecules [36]. These isolated cellulose microfibers are composed of a linear polymer of D-glucose units linked through 1,4-glycosidic bonds. In plants, the microfibers contain highly crystalline regions of exclusively cellulose I, a parallel arrangement of cellulose chains held together by hydrogen bonding, that are separated by amorphous regions [37]. Cellulose microfibers can be 2–20 nm in diameter and tens of microns long [36].

In 1951, Rånby developed a method to isolate the crystalline regions of cellulose microfibers through acid hydrolysis [38]. Exposing the cellulose microfibers to mild acidic conditions selectively degrades the amorphous regions in the microfibers, thereby yielding rod-shaped CNCs (Fig. 1). Isolated CNC rods can vary between 50 to 2000 nm in length depending on the biological source from which they are extracted [32]. For example, CNC rods from wood and cotton have diameters of 5 to 10 nm and are 100 to 200 nm long, whereas CNC extracted from algae and tunicates can have lengths of 1000 to 2000 nm. Extraction of CNCs using sulfuric acid is the most investigated preparative method because hydroxyl groups on the CNC rods are partially converted into sulfate esters during hydrolysis. The introduction of these negative sulfate surface groups helps stabilize aqueous dispersions of CNCs through electrostatic repulsion.

The lyotropic liquid crystalline phase of a colloidal CNC suspension was first reported in 1959 by Marchessault et al. [39]; the chiral nematic phase, however, was not identified until 1992 by Gray and co-workers [29*]. Analyzing CNCs extracted from wood microfibers using sulfuric acid, Gray and coworkers demonstrated that CNCs form chiral nematic liquid crystals (LCs) above a critical concentration (Fig. 1). The CNC rods act as LC mesogens and align along their long molecular axis. In the simplest case, this alignment would lead to a nematic phase with long-range orientational order but no positional ordering. Chirality can be introduced into the nematic system causing an intrinsic helical twist perpendicular to the long axis of the mesogens [40]. In the case of CNCs, only left-handed (LH) chiral nematic structures have been observed.

CNC films obtained through evaporation-induced self-assembly (EISA) retain the chiral nematic structure of the CNC rods [41]. The CNC films contain three different levels of chirality: (1) chirality at the molecular level attributed to asymmetric carbon atoms in the D-glucose subunits; (2) chirality of the twisted morphology of the individual CNC rods; and (3) chiral nematic ordering of the LC. This long-range chiral nematic ordering imparts photonic properties on the CNC films. Photonic crystals are materials that have periodic layers with different refractive indices, leading them to selectively diffract light of a wavelength on the order of the layer spacing. The relationship between the wavelength reflected (λ_{max}) by the chiral nematic structure, refractive index (n_{avg}) and helical pitch (P) can be described by the following equation: $\lambda_{max} = n_{avg}P\sin\theta$ (Fig. 1) [42]. Only light with a circular polarization that matches the handedness of the helical structure is reflected; thus, CNC films reflect only LH circularly polarized light since they have LH organization. As the helical pitch of the CNC films is on the order of microns, the reflected light can range from the ultra-violet through visible and to near-IR wavelengths.
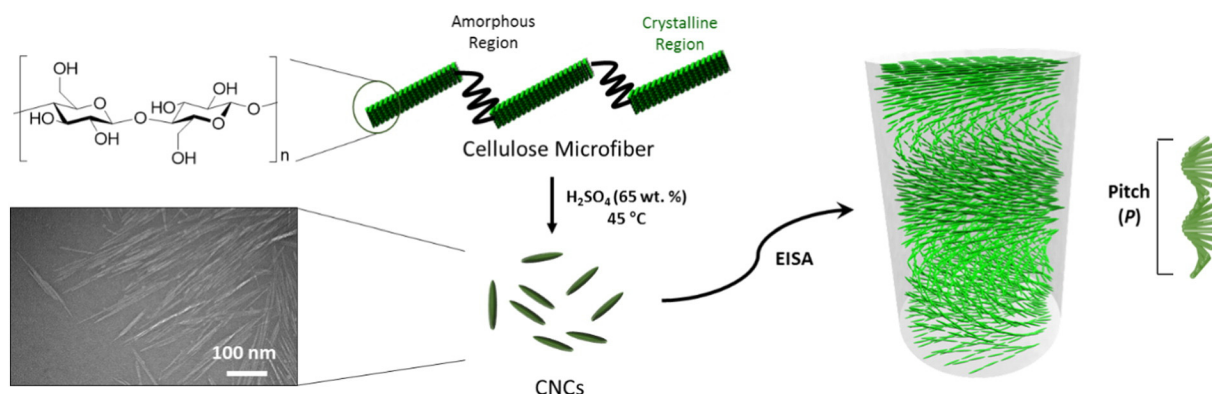

Fig. 1. Schematic for the extraction of CNCs from cellulose microfibers by acid hydrolysis. Bottom left: negatively stained transmission electron micrograph of CNCs.