



Behavior of nanocelluloses at interfaces



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ABSTRACT

Despite being non-surface active, nanocelluloses position efficiently at interfaces, already at very low concentration. This behavior has lately triggered a strong interest in the cellulose and colloids communities. This review reports the recent developments on the use of nanocelluloses at interfaces and highlights the fundamental principles governing the high efficiency observed in reinforcing the boundary between two phases. The use of nanocelluloses as emulsifier and emulsion stabilizer is first discussed, and the structural properties of nanocelluloses such as aspect ratio and surface properties are correlated with the high efficiency in forming colloiddally-stable multiphase systems. Then, the behavior at the air/water interface is presented and the most recent advances are reviewed with focus on the surface free energy of nanocelluloses and their role in the interfacial self-assembly process.

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1. Introduction

In addition to the early and more straightforward use of nanocelluloses as reinforcing agent in composites, owing to its fibril nature, a trend has grown towards the study of nanocellulose as a colloid. By extension, the interest in understanding the behavior of cellulosic nanofibers in mixed systems has also emerged. Their ability to stabilize interfaces has been in the focus during the last decade as it amplifies the possibilities for material design by moving towards emulsions and foams. One of the reasons of this interest is of technological nature as emulsions and foams constitute ubiquitous materials well anchored in the consumers' needs in pharmaceuticals, cosmetics, paint, etc. As the particles can assemble at interfaces (gas/liquid or liquid/liquid), they the coalescence of the dispersed phase by steric hindrance or electrostatic interactions. In comparison to many other types of particles, nanocelluloses are abundant, sustainable, they display high surface area, low mass density, chirality, easy surface modification and excellent thermo-mechanical performance. In addition, they are considered as environmentally benign and pose no or minor risk for the living organisms.

Nanocelluloses can be issued from a variety of natural sources (vegetal, bacterial or animal) and processes (enzymatic, chemical, mechanic). They consequently appear under a large range of shapes, aspect ratio,

surface chemistry, crystallinity, and crystalline structure ($I\alpha/I\beta$ ratio) [1–3]. Above all the differences that are induced by the extraction route, they can be divided into two main types. The longer semi-crystalline elementary fibrils, also called cellulose nanofibers (CNF), can reach several microns in length. CNF is the main source of nanocellulose and comprises both crystalline and amorphous domains. The crystalline domains may be isolated from CNF leading to the so-called cellulose nanocrystals (CNC). The high degree of crystallinity combined with their small dimensions make CNC the smallest building block of the cellulose fibers; despite the inherent variability in size, a length between 70 nm up to a few microns and a width between 5 and 20 nm are typically cited [2]. These dimensions (its high aspect ratio) make CNC a rigid, rod-like nanoparticle. In turn, these features have important consequences on the interfacial behavior, as will be discussed throughout this review. Furthermore, the increasing number of commercial sources has boosted their possible uses, allowing the emergence of new applications.

Since the pioneering observations by Ramsden and Pickering about the effect of particles at interfaces in 1903 and 1907, respectively [4,5], their role in the stabilization of emulsions and foams is still a subject of current research. It has taken nearly 90 years for the community to start to rationalize the bases for particle behavior at interfaces. More recently, Binks, Leal-Calderon, Schmitt and many others [6,7], have expanded this field. Two parameters are currently recognized as crucial in governing the assembly and adsorption process: the surface chemistry of the particles, and their shape. Whereas major efforts have been conducted with isotropic particles, i.e., spheres, the work on anisotropic particles has originally begun with two-dimensional particles, for

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instance clays and more generally flat particles [8–10] (Fig. 1, k, l). The use of rod-like particles, with high aspect ratio, reduces to 1 the dimension of the particle. The fibril nature of the cellulosic nanomaterials fits well this trend as the large range of available morphologies offers good case studies [11,12], see Fig. 1, a–j. Fig. 1m, illustrates the more limited assembly of spherical particles at the surface of a droplet.

Here we report the current state of the art regarding nanocelluloses and their behavior at interfaces, namely liquid/liquid and gas/liquid interfaces, and illustrate how they permit the design of materials with tailored properties. Based on current trends, we also suggest how

controlling nanocelluloses at interfaces could be one of the keys to enable a generalized approach towards material development.

2. Nanocelluloses: towards 1d particles

Cellulose biosynthesis is unidirectional. Hydrogen bonds promote stacking of multiple cellulose chains forming cellulose sheets that further aggregate into larger nanofibrils by van der Waals interactions and with dimensions varying from 5 to 50 nm in diameter and several microns in length, depending on the source of cellulose. The hierarchical nature of the material is shown Fig. 2. This results in nanocelluloses

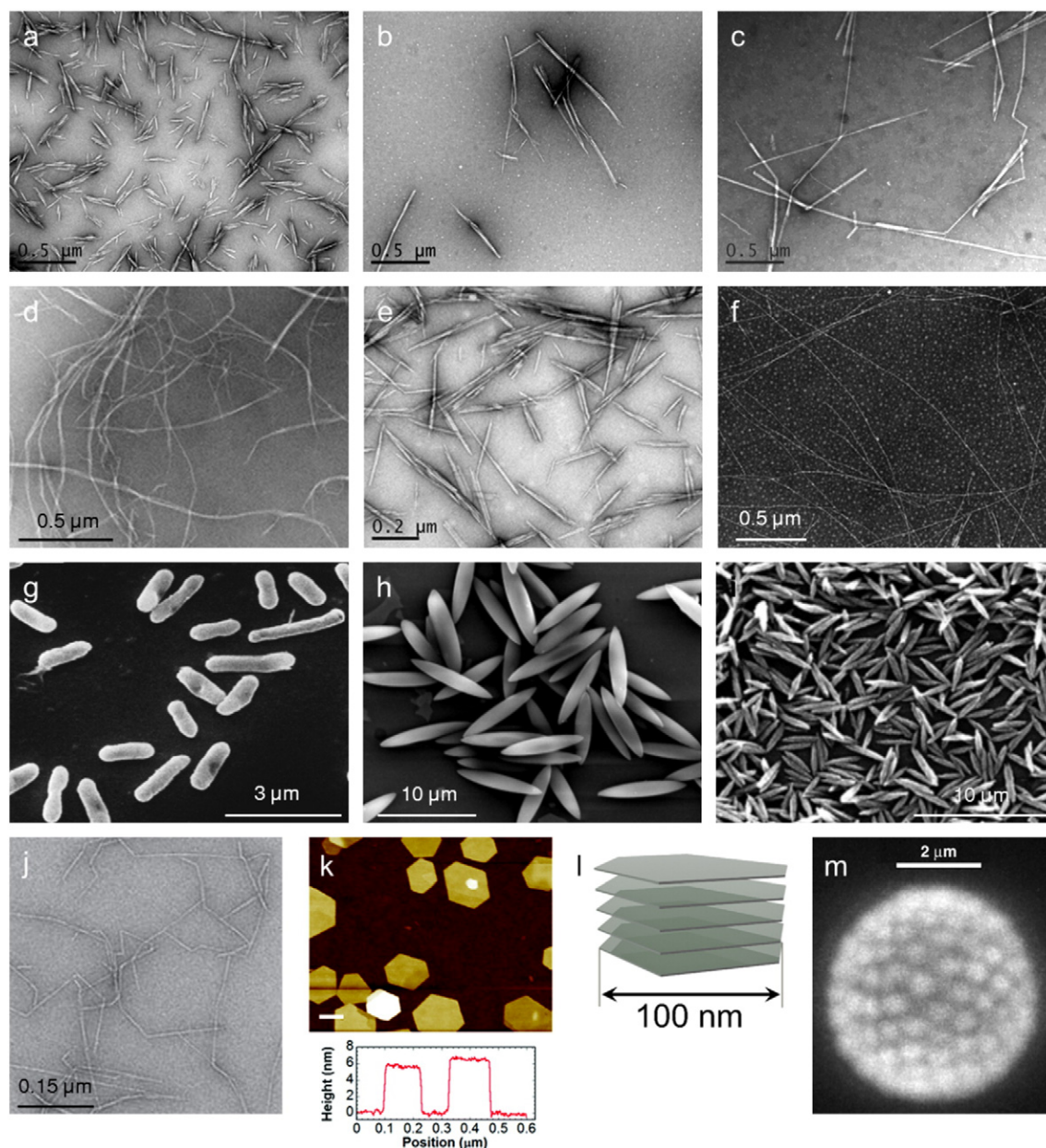


Fig. 1. Images of various particles: CNC obtained from (a) cotton, (b) bacterial cellulose and (c) *Cladophora* (from [12] – reproduced by permission of The Royal Society of Chemistry), (d) wood CNF (reprinted with permission from [13]. Copyright 2014 American Chemical Society) (e) Chitin nanocrystals issued from crab (reprinted with permission from [14]. Copyright 2014 American Chemical Society), (f) heat-induced β -lactoglobulin fibers diluted to 0.1% in water at pH 2 (reprinted with permission from [15]. Copyright 2014 American Chemical Society), (g) *E. coli* DH5 bacteria that have interfacial activity when associated to chitosan (reprinted with permission from [16]. Copyright 2012 American Chemical Society), and hand-made anisotropic nanoparticles (h) charged polystyrene particles with an aspect ratio of 5.3, obtained from 3.1 μm spheres deformed embedded in a PVA film (reprinted with permission from [17]. Copyright 2009 American Chemical Society) and (i) Spindle-like hematite particles ($\alpha\text{-Fe}_2\text{O}_3$) synthesized by hydrolysis of iron(III) perchlorate (adapted from [18] – reproduced by permission of The Royal Society of Chemistry). (j) TEMPO oxidized CNF (from [19]), (k, l) montmorillonite and its corresponding schematic structure (scale bar = 100 nm, adapted from [20,21] – reproduced by permission of The Royal Society of Chemistry) and (m) projection of a three-dimensional confocal fluorescence microscope image of 0.7- μm -diameter PMMA colloidal particles adsorbed onto the surface of a water droplet in decalin (adapted with permission from [22]).

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