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Adsorption and Assembly of Cellulosic and Lignin Colloids at Oil/Water Interfaces

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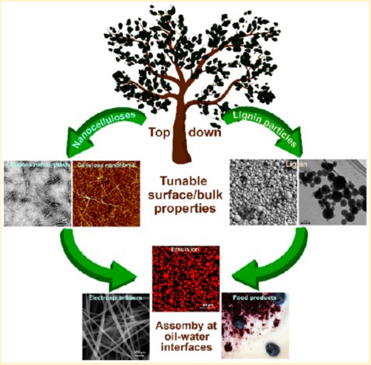
ABSTRACT: The surface chemistry and adsorption behavior of submicrometer cellulosic and lignin particles have drawn wide-ranging interest in the scientific community. Here, we introduce their assembly at fluid/fluid interfaces in Pickering systems and discuss their role in reducing the oil/water interfacial tension, limiting flocculation and coalescence, and endowing given functional properties. We discuss the stabilization of multiphase systems by cellulosic and lignin colloids and the opportunities for their adoption. They can be used alone, as dual components, or in combination with amphiphilic molecules for the design of multiphase systems relevant to household products, paints, coatings, pharmaceutical, foodstuff, and cosmetic formulations. This invited feature article summarizes some of our work and that of colleagues to introduce the readers to this fascinating and topical area.



CELLULOSIC AND LIGNIN COLLOIDS

Cellulosic and lignin colloids are feasible solutions to the pressing need to adopt sustainable materials, for example, by exploiting their inherent physicochemical properties, especially considering their ability to form (supra)colloidal structures. Such aspects are central to the scope of *Langmuir*; therefore, this article introduces such plant-based materials in current developments involving fluid/fluid interfacial stabilization.

In plants, cellulose is the main load-bearing component, forming semiordered microfibrils. Lignin, on the other hand, is often considered to "act as a glue" between the fibrils and fibers. This is, however, an oversimplification because other functions are equally important. Lignin is mostly derived from plants, while sources of cellulose also include bacterial biofilms and sea animals.

Among the various cellulosic materials, the recent popularity of nanocelluloses stems in part from their fibrillar or rodlike nature, nanometer size in the lateral dimension, tailorable crystallinity, and structuring capabilities, which equip them for a vast number of applications. We consider two basic types of nanocellulose, rodlike cellulose nanocrystal (CNC) and cellulose nanofibril (CNF), where the latter displays a higher axial aspect. They contain ordered structures with packed parallel cellulose chains that form a dense network held together by van der Waals and hydrogen bonding interactions.

To keep the internal native crystalline structure, the most common route to access nanocelluloses is by disintegration of the plant cell walls. Thus, unlike most synthetic nanoparticles, most nanocelluloses are produced top-down and preserve, to some degree, the biologically derived morphology and ordered structure of cellulose in plant cells. Therefore, the processing method greatly influences their characteristics, including dimensions, composition, molecular integrity, and crystallinity, among other properties.

One may think that the interactions involving nanocelluloses in their native or isolated forms are well-understood; however, this is far from true. The same holds for the second component considered here, lignin. Because of the growing interest in using biobased colloids, several aspects need to be addressed with regard to the structures, self-assembly, interactions, and applications of nanocellulosic and lignin particles. As for the former, their building block, the cellulose macromolecule, may be deemed uninteresting given its apparent simplicity as a linear homopolymer comprising C, O, and H atoms. A very different perception arises when it comes to the way it assembles in hierarchical and multiscale structures. In contrast, lignins are heterogeneous and complex macromolecules. Several questions arise relative to the native or isolated forms of nanocellulose and lignin:

(1) How do the structures they form evolve in nature to respond to the multiple demands of living organisms? Can such designs be engineered into new materials after their cleavage from the cell walls of fibers, following suitable deconstruction protocols?

(2) What type of structures do cellulose chains make in the native or never-dried forms?[1] Do the structures involve ordered regions alternating with less ordered domains? In addition, in regards to lignin, are the isolated structures branched or not? What type of assemblies do they form?

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(3) If we consider both cellulose and lignin, what is the nature of their interactions in the cell wall? And how do such interactions play once they are isolated and/or combined in a given multiphase system? What is the role of hydrophobic interactions that determine the insolubility of cellulosic structures in water?[2,3] Likewise, in the case of colloidal lignin, what is the nature of their interactions in liquid media?

(4) Combined in the cell walls of plants, cellulose and lignin form an intricate composite that sustains mechanical, thermal, biological, and environmental stresses (fire, water, pathogens, etc.). Do they lose such features when separated and used as a single component, for example, in a solid material or in an emulsion? Alternatively, once isolated, is it possible to restore some of the properties observed in the original fiber precursors? This last question has been partially addressed in the context of solid composites. However, for liquid/liquid or multiphase systems, this remains an open question.

After isolation, the large density of hydroxyl groups in nanocellulose and lignin provides ample possibilities for functionalization, using conventional water- and alcohol-based chemistries.[4] In addition, both nanocelluloses and lignin particles display nonspecific interactions with cellulose derivatives. This facilitates hybridization and multicomponent materials to be formed. Several reviews covering a wide range of aspects related to nanocelluloses are available, including those from our group.[5−11] In fact, *Langmuir* has published a couple of relevant, complementary Invited Feature Articles (see refs 12 and 13). The first reference compared the characteristics and properties of lab-made and industrial nanocelluloses, enticing a growing "optimism" for their deployment in colloidal systems.[12] The second reference discussed the generic use of colloidal particles in a range of fluid/fluid interfaces.[13] Here we expand on the construction of supramolecular assemblies at fluid interfaces, a field that is in the early stages. Lignin colloids are reported less frequently: while many studies are available regarding their isolation, characterization, and modification, very limited knowledge exists regarding their structuring and colloidal behaviors in aqueous suspension, an issue that is covered here, at least partially.

The design, isolation, and use of nano- and microparticles are relevant to a broad spectrum of interdisciplinary fields, spanning from food to advanced electronics.[10,14−16] They have been utilized as models to understand the principles that govern interactions that typically occur in nature. Therein, a remarkable complexity exists, given the hierarchical, multiscale, and multicomponent features of biological systems.

Cellulose Nanofibrils. The most readily available source of nanocelluloses and lignins are plants, wood, and forest products as well as side streams generated during their processing. Within nanocelluloses, CNFs are usually obtained by disintegrating the fibers' cell walls by strong mechanical shear, following appropriate pretreatments, e.g., selective acid and enzymatic hydrolysis[17,18] or chemical oxidation. For instance, catalyzed oxidation is one of the few processes that isolates truly individual CNF, such as TEMPO (2,2,6,6-tetramethyl piperidine-1-oxyl radical)-oxidized nanocelluloses,[19] which display uniform lateral dimensions. By contrast, intensive mechanical shearing results in a more heterogeneous distribution of the lateral dimensions of CNF. The relatively high axial ratio of CNF, coupled with its flexibility, promotes entanglements that together with hydration and electrostatic interactions (if present), trigger the formation of hydrogels at very low concentrations.

Cellulose Nanocrystals. CNC is typically produced by controlled acid hydrolysis that selectively targets the disordered cellulose segments present in the source material, leaving the crystallites intact.[20] The resultant nanoparticles are rigid nanorods of highly ordered (crystalline) cellulose. The most common CNC preparation method, via sulfuric acid hydrolysis, installs charged half-ester sulfate groups on the CNC surfaces and ensures their excellent colloidal stability in aqueous media. Resulting from CNC's inherent chirality or handedness, it self-assembles into chiral nematic liquid crystal phases.

Lignins. Generally, lignin is removed during isolation of fibers. However, it has been realized that many advantages may materialize if (residual) lignin remains in the isolated "ligno-nanocelluloses". Indeed, this enables some level of control on their interactions with water, depending on the composition and type of lignin (which depends on the precursor plant source).[21−24] Thus, we propose that consideration should be given to (1) lignocellulosic colloids (colloids containing cellulose and bound lignin), (2) those inherently produced as mixtures containing nanocellulose and lignin, and (3) colloids that combine the single components (isolated nanocelluloses and lignins derived from the same or different sources). It is for this reason that we discuss both nanocelluloses and colloidal lignins separately but with an appreciation for new possible uses if they are recombined strategically.

The recent progress in green, plant-based colloids is swiftly attracting increased interest in both academia and industry. Here we introduce the subject with special emphasis on results from our recent work dealing with the development of multiphase systems, particularly for the stabilization of oil/water interfaces. The colloidal stability and parameters affecting such properties are all important when formulating emulsions. In addition, the size, geometry, and morphology of plant-based colloids provide new insights and opportunities to address emerging applications. We highlight a range of uses for plant-based colloids: in helping to minimize the use of petroleum-based substances, in endowing mechanical strength, in reducing materials' cost, and in developing advanced green materials. Our anticipation is that this discussion will trigger ideas for the development of new platforms with impact in colloidal and material systems. Finally, it is feasible that new opportunities may emerge by taking advantage of the synergies between nanocelluloses and lignins.

■ KEY ADSORPTIVE FEATURES OF PLANT-BASED COLLOIDS

Relevant to this contribution is the fact that phenomena such as stability, surface reactions, and mobility play critical roles in determining the behavior and fate of colloidal particles, whether they are of synthetic or natural origins. A main emphasis of our work is the introduction of plant-based colloids in the stabilization of multiphase systems, particularly the emulsion's oil/water interfaces. The associated processes and the state of dispersion are principally regulated by the nature of the colloidal particles and the conditions of the surrounding medium as well as the presence of dissolved substances.[25] At the oil/water interface, ionic strength and pH affect the surface charge of the adsorbed particles, defining the activity and the stability of the multiphase system,[13] which can be further tailored by steric interactions, especially in the presence of adsorbed, soft polymeric layers.[26]

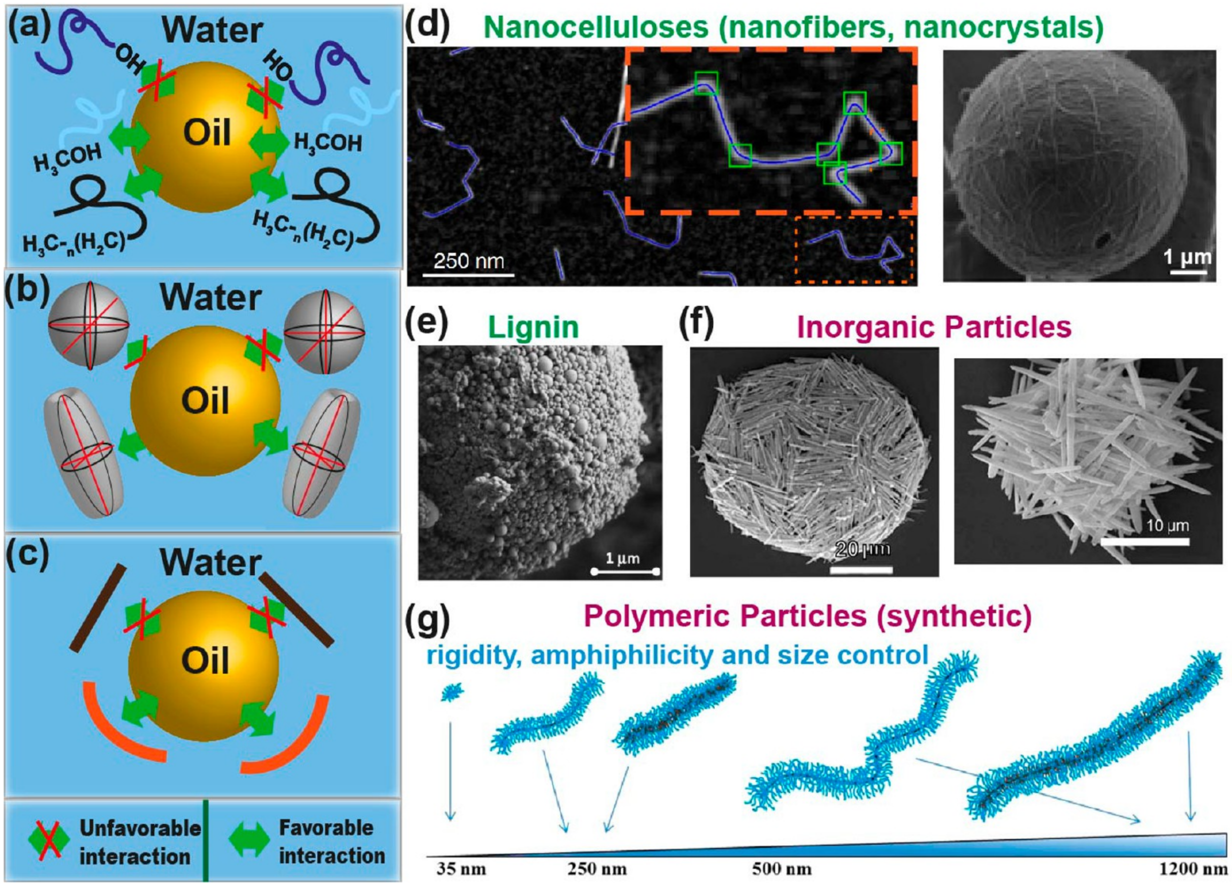

Figure 1. Examples of biomass-derived, inorganic, and synthetic particles. (a) Characteristic chemical groups present on solid particles and interactions with a nonpolar oil affecting adsorption. (b) Adsorbed particle anisotropy and (c) flexibility favors both interactions and structuring (close packing) at the interface. (d) (left) Cellulose nanofibril (CNF) adsorbed on a flat surface showing flexible domains and kinks (see small squares) with the crystal domains limiting their flexibility. Adapted with permission from ref 35. Copyright 2015 Springer Nature. (right) Highly packed CNFs adsorbed at curved interfaces. Reproduced with permission from ref 45. Copyright 2013 Royal Society of Chemistry. (e) An oil droplet is shown fully covered with adsorbed lignin particles. Reproduced from ref 46. Copyright 2016 American Chemical Society. (f) Rigid inorganic particles assembled on small (right) or large (left) bubbles. Reproduced with permission from ref 36. Copyright 2009 Wiley-VCH. (g) Illustration of synthetic bottle-brush polymers where the flexibility, amphiphilicity, and size can be easily controlled over a large range. Reproduced from ref 47. Copyright 2015 American Chemical Society.

In nature, solid composite assemblies are often joined by covalent and noncovalent bonds that modulate their dynamic changes and rearrangements.[27,28] The case of fluid interfaces is less common in natural system but of high technological relevance. Here, the adsorption strength of natural colloids at fluid interfaces is largely associated with the ability of a given fluid to wet the surface of the particles.[13] Thus, a key advantage of utilizing plant-based colloids is the possibility of selected chemistries and reaction conditions that can be introduced during their isolation, conducted either by bottom-up or top-down approaches. Importantly, the geometry and morphology of the particles are to be considered as additional, critical parameters that significantly modulate their functions.[29,30] When evaluating the physicochemical properties of colloids interacting at the oil/water interface, several aspects come into play, including (i) the balance of interaction energies of the particle at the oil/water interphase, (ii) particle's adsorbed conformation at the interface, and (iii) the relative magnitude of interfacial area covered by the particles relative to their size or volume (Figure 1a−c). Accordingly, the interactions between the particles and the given phases are favored by the right hydrophilic−hydrophobic balance, which is dictated by the inherent surface chemistry, the particle's dimensional anisotropy, and the molecular and colloidal flexibility.[9]

Adsorption of Nanocelluloses. The wide choice of plant-based colloid morphology and rigidity can be conveniently selected, depending on their origin and method used for their isolation. Also, their surface chemistry can be easily altered. Apart from their eco-friendliness and bio/economic integration, they offer unique properties compared to conventional, synthetic colloids (those produced from metals and minerals or petroleum-based polymers). Still, significant challenges need to be addressed for interfacial stabilization when adopting biocolloids, also including other polysaccharides, proteins, extractives, and biogenic minerals.

Compared to petroleum-based particles, nanocelluloses possess relatively high thermal stability and insulation properties,[31] which can be attributed to their density, width, and cross-sectional area[32] and the orientation of the crystalline axis. Nanocelluloses are also chemically resistant to the vast majority of organic solvents.[33] Concurrently, both nanocellulose and lignins undergo degradation through biochemical pathways.[34] Moreover, their biodegradability highlights an effective solution to current problems that are otherwise faced when using, for

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instance, latexes that in the long run pose environmental concern.

Nanocelluloses, as the principal plant-based source for anisotropic particles, are quasi 1D, high aspect ratio nanofibrils (widths down to the nanometer levels and lengths that can reach several micrometers). Their flexibility is limited to the crystalline domain of the fibrils with sizes in the order of 10^2 nm (Figure 1d).[35] Taking these features together, it has been postulated that nanocelluloses are ideal choices for oil/water interfacial interactions as long as the radius of curvature of the interface is at least above half the length of the crystalline domains within the nanocellulose.[36,37] For example, interfaces with a radius of curvature in the micrometer scale, onto which CNCs were self-assembled, showed a relatively tight packing (Figure 1d, right). CNC has outstanding axial elastic modulus (Figure 1d, insert), and indirect observations (experimental and computational) reveal the presence of crystal faces that differ in their density of OH groups or hydrophilicity.[38] This expands the possibility for interactions at interfaces but in a manner that is not fully understood; for instance, CNC interacts readily with and stabilizes the oil/water interface, whereas it does not present significant surface (air/water) activity. A plausible explanation is that the surface potential of the air/water interface has an anionic character above pH 4, thus limiting adsorption of negatively charged CNC in conventional conditions.[39] Interestingly, the inherent interparticle electrostatic repulsions do not affect CNC interaction at the air/water interface, for instance, in the assembly of highly packed layers constructed by different deposition techniques, as shown by us,[40,41] and even in conditions above the kinetic arrest concentration.[42] Some clues for the elucidation of the structure of CNC and its potential interaction in an aqueous environment may be given by its polymeric nature that contrasts, for instance, with inorganic particles. For example, polymers such as poly(ethylene glycol) clearly exhibit H-bonding with CNC in the dry state, but the interaction in the wet state is limited.[43] If one takes as an example the surface interactions of polystyrene particles with other multimeric compounds, they are simply explained by the chemical nature of the polymer.[44] This effect, however, may be limited given the crystalline and highly ordered nature of CNC.

Adsorption of Colloidal Lignin. In contrast to typical nanocelluloses, nonfibrillar, spherical, and nano- and microparticles can be produced from lignin.[17,48] Other plant-derived particles can include biogenic silica[49] and those produced after cellulose regeneration.[50] Lignin particles can be prepared from industrial side streams by using a number of methodologies. They are generally designed to be spherical; therefore, their interaction at the oil/water interface follows previous findings for particles of synthetic origin with the same shape (Figure 1e). The interaction of lignin macromolecules with a given solvent depends on factors such as ionic strength, pH, temperature, solvent quality, and, importantly, monolignol composition in the lignin.[51] In most solvents, lignin is mostly found as associated structures, for example, in the form of cylindrical building blocks having 4−10 monolignol units, where the amount of monomers per building block is influenced by lignin concentration.[51] An attractive aspect of lignins is their versatility because they can be obtained with given chemical composition, molar mass, and solvent affinity, depending on their source and separation process.[52] While this can be upsetting for cracking the macromolecule into monomeric precursors, it is an advantage in the domain of colloid science, as a toolbox with a variety of choices as far as the expected interfacial behaviors.

Comparison with Nonbiobased, Synthetic Colloidal Systems. The library of available options is rather large if one considers the currently available nonbiobased, synthetic particles (either organic or inorganic), which have been designed to adsorb at the oil/water interface, principally in Pickering systems. The synthesis of anisotropic organic and inorganic particles has been expanding, for several decades now, following progress of surface chemistry to control their morphological properties. An example is that of spherical silica or latex particles that have been used for nearly a century. Highly reproducible and facile synthetic protocols have been developed for the fabrication of spherical particles, but this is quite different in the case of anisotropic ones, which demand considerably more tedious processes. Compared to plant-based particles, a significant drawback of the synthetic counterparts is their expected nonbiodegradability. In some cases, they can also be a toxicological hazard to humans, directly or indirectly, for example, via the food chain. Related effects are being evaluated for plant-based materials, and so far they have been found not to elicit immune reactions, even after prolonged exposure after introduction intracutaneously in model animals.[53] The biocompatibility of materials formed from nanocelluloses can be a significant advantage compared to typical synthetic systems.[54,55]

High surface area, multifunctionality, and controlled network structuring are easily obtainable with synthetic particles owing to the bottom-up synthesis where the process itself can be adjusted in terms of the monomeric precursor, the initiator and, if applicable, the emulsifier used (e.g., in latexes).[56] This is in contrast to natural organic colloids that comprise a polymeric backbone, when extracted from plants or obtained from bacteria. Additionally, synthetic particles can be obtained in sizes ranging from a few nanometers to several micrometers, whereas the range of dimensions of plant-based colloids is somewhat limited by the source; moreover, they are inherently polydisperse.[14,46,50]

Anisotropic inorganic particles are generally obtained with sizes <1 μm, commonly synthesized from building blocks such as silicates, gold, or metal-oxides. They find use in the stabilization of interfaces and outperform spherical particles because of their higher contact area relative to their mass or volume (Figure 1f). Nevertheless, those particles are rigid in nature and cannot conform to any given surface.[30] When the length of such inorganic nanoparticles becomes considerable in comparison to the radius of curvature of the interface, a smooth adsorbed layer cannot be attained and "hedgehog"-type structures result, with the particles organizing tangentially to the interface.[44] Therefore, controlling the source of nanocelluloses and the size of the crystalline domains offers the possibility to tether interfacial adsorption that cannot yet be achieved with inorganic systems.[11]

Synthetic anisotropic particles obtained from organic materials, mainly polymers, are generally obtained with sizes above one micrometer except for oblong micellar assemblies, bottle-brush polymer particles, and replica particles obtained from inorganic templates. These have been used only scarcely for the stabilization of interfaces but have found applications principally as biofunctional particles and rheology modifiers. Polymeric bottle-brush architectures are a good example of a versatility that is not yet available from plant-based particles. For instance, the aspect ratio of bottle-brush polymers, their size (from nanometers to several micrometers), functionality, responsiveness, and flexibility can all be engineered at once, subsequently highlighting an extremely high degree of versatility as a result of a long history of developments in synthetic

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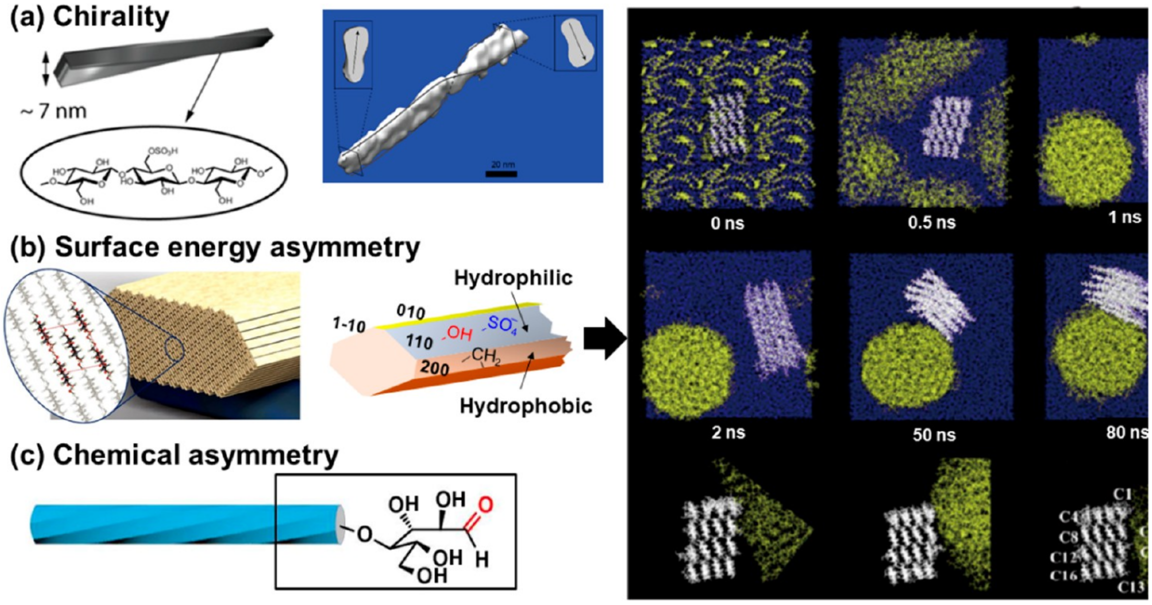

Figure 2. (a) Schematic illustration and electron tomography image of twisted (chirality) CNC with 7 nm diameter and bearing surface hydroxide and half-ester sulfate groups. Reproduced from ref 60. Copyright 2014 American Chemical Society. (b) Left: different planes of CNC with given levels of hydrophilicity. Adapted with permission from refs 63 and 69. Copyright American Chemical Society 2012 and Tappi Press 2013, respectively. Right: snapshots at different times in a molecular dynamics simulation to indicate the configuration of CNC (see packed cellulose chains in white) in a two-phase medium comprising octane (yellow) and water (blue). Adapted with permission from ref 66. Copyright 2017 Taylor & Francis. (c) Illustration of chemical asymmetry of CNC, showing reducing end on the right of a CNC rod. Reproduced with permission from refs 67 and 68. Copyright 2013 and 2014 American Chemical Society and Springer Nature, respectively.

chemistry (Figure 1g).[47] Therefore, although not fully studied yet, all of these qualities are expected to allow control of interfacial interactions.

To fulfill an increasing demand for sustainable materials, plant-based colloids have been isolated or designed to exploit some of their unique physicochemical properties, while suppressing the production cost and promoting eco-friendliness. Although fine process engineering is required for large-scale production, isolation of plant-based colloids can benefit from the adoption of green routes[17] and relatively low production costs, as we reported recently for CNC,[57] CNF,[58] and lignin nano- and microparticles.[59] Moreover, considerably less tedious procedures are used to obtain nanocellulose and lignin colloids than, for instance, the bottle-brush systems just discussed.

■ BIOBASED COLLOIDS AT FLUID/FLUID INTERFACES

Morphological and Surface Features. Fascinating aspects of nanocelluloses, which attract considerable attention, are their tailorable fibrous morphology and surface properties. Cellulosic particles isolated from different sources, following given methods, display various sizes and axial length ratios which can induce special structuring and adsorption behaviors. This is not the case of colloidal lignin, mostly forming spherical morphologies. Remarkably, CNC displays an intrinsic right-handed chiral twist (Figure 2a, left), enabling it to form liquid crystals above a given concentration, depending on its aspect ratio, crystallinity, and surface charges.[42] The helicoidal twist along its longitudinal direction has been directly proved by electron tomography (Figure 2a, right).[60] Furthermore, in given conditions and upon drying from aqueous dispersion, CNCs preserve their initial self-assembled, cholesteric nematic phases and produce photonic band gaps in the visible region due to the twisted rodlike shape and anisotropic charge distribution.[42] The chirality of crystalline cellulose provides great opportunities for functional and advanced applications of CNC in structured assemblies.

The surface hydroxyl groups of CNC and CNF are regarded as nonsurface-active.[9] Nevertheless, the potential of nanocellulose to self-assemble at the oil/water interface has been successfully exploited in a variety of applications, both of fundamental and practical importance.[10] In the context of this invited feature article, it is critical to understand the characteristics and dynamic behavior of nanocelluloses at the oil/water interface. One of the major factors that dictates their behavior at interfaces is how they achieve interfacial adsorption or attachment to the nonpolar phase (oil). The crystalline faces of nanocelluloses are structurally nonequivalent, showing one with a partial hydrophobic character.[11,61] Capron et al. found that the amphiphilic character of CNC, observed for the Iα and Iβ cellulose lattices, relied on the (200)β/(220)α hydrophobic edge plane. Therefore, CNC could adsorb with this less polar crystalline plane for which axial CH moieties are directly exposed at an edge truncation at the surface of the crystal.[62] Thus, the wettability of CNC at the oil/water interface is controlled by their crystalline orientation (Figure 2b, left), that is, the hydrophobic (200) edge is expected to orient toward the oil phase.[63] Moreover, a recent study investigated the relationship between bending characteristics for all plane directions of CNC.[64] It was found that the bending angle that reached the plastic deformation limit was approximately 60° in all directions, and particularly, the (200) crystalline plane presented higher bending potential compared with the others. This finding provides evidence that the specific crystalline plane of CNC can bend along the oil/water interface, that is, the small deformation of CNC, accommodating to the curvature of oil droplets, promotes interfacial wetting and adsorption.

One question that emerges is still how nanocelluloses dynamically interact at the oil/water interface. This was investigated by using small-angle neutron scattering (SANS),[65] which suggested that CNC adsorbed as monolayers with varying surface density, mainly depending on interparticle interactions. Interfacial multilayers can also be formed if the CNC bears no charges, for example, after desulfation of CNC produced via sulfuric acid hydrolysis. Furthermore, the neutron wave vector dependence with the intensity showed that CNCs were in contact with the oil only via their surfaces but did not penetrate the bulk phase; no deformation of the oil surface at a nanometer scale was revealed. The results reinforce the hypothesis that the (200) crystalline plane of CNC directly interacts with oil and clarifies that the interaction is limited to interfacial contact. Similar interfacial contact behavior of CNC at the oil/water interface has been shown by molecular modeling (Figure 2b, right panel).[66]

CNC can be easily modified using numerous reactions,[11] and it is possible to take advantage of an interesting property: CNC's cellulose chains are arranged in a parallel configuration, resulting in crystals bearing reducing and nonreducing end groups. Such chemical anisotropy, as far as the difference in reactivity of the ends of the crystal,[67] allows for asymmetrical or end-selective modification (Figure 2c). An efficient chemical route to introduce chemically versatile thiol groups at the reducing ends of CNC was reported by us.[68] Thiolation of CNC at the reducing end was carried out by first carboxylation of the reducing end aldehyde groups followed by reaction with *N*-hydroxysuccinimide-1-ethyl-3-(3-dimethylamino) propyl carbodiimide (NHS/EDC-mediated activation) and final reaction with nucleophilic amine molecules carrying thiol termini. The selectivity and extent of thiolation at the reducing end of CNC were confirmed by transmission electron microscopy imaging of silver nanoparticles that tagged the CNC termini. These results revealed the inherent chemical asymmetry of CNC and presented a precise control over CNC self-assembly behavior on surfaces, broadening the applicability of CNC in versatile technologies.

Droplet Stabilization. The effect of elongated shapes of nanocelluloses on their interfacial adsorption has been reported for hexadecane and water.[45] Nanorods with lengths ranging from 185 nm to 4 μm (aspect ratios ranging from ca. 13 to 160), were found to irreversibly adsorb at the oil/water interface. The formed oil droplets showed similar diameter, indicating that CNCs presented roughly the same interfacial wetting properties as well as flexibility at interfaces. The aspect ratio more directly influenced the interfacial coverage on the oil droplets, that is, CNCs with small aspect ratio formed a dense layer (coverage >80%) while an interconnected network of low coverage (40%) took place for the longer nanorods (Figure 3a). Furthermore, the shorter nanocrystals were shown to promote individual droplets, whereas longer nanorods were involved in networked structures. In fact, more than half of the introduced, 4 μm nanorods were involved in the formation of the interfacial network; meaning that a substantial proportion formed extended bridges between adjacent droplets (Figure 3b), again demonstrating that the aspect ratio significantly affects the adsorption of nanocelluloses at interfaces. The results lead to a better understanding of adsorption for rodlike particles of given sizes and to the elaboration of controlled surface architectures, from a homogeneous monolayer to interconnected porous multilayered interfaces.

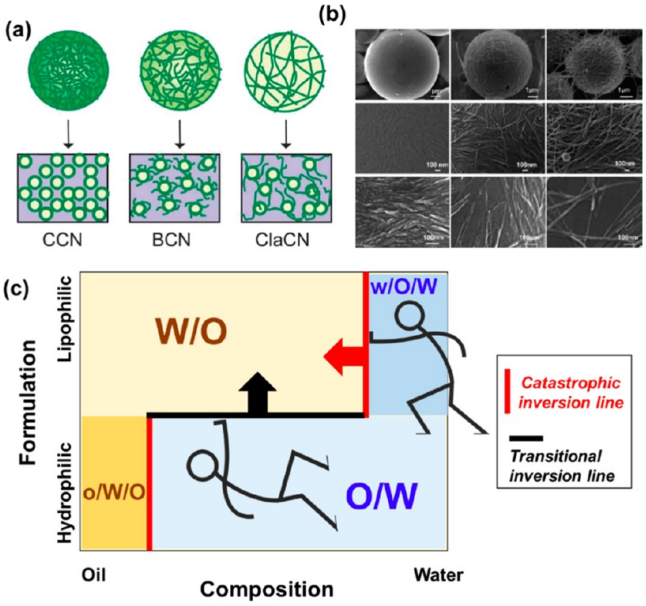

Figure 3. (a) Schematic representation of droplets with adsorbed CNC of different axial ratio: CCN (cotton-based CNC, left), BCN (bacterial-based CNC, middle), and ClaCN (Cladophpra-based CNC, right). Individual droplets (top) and the Pickering emulsion system (bottom) are shown. (b) Scanning electron microscopy (SEM) images of polymerized styrene−water emulsions stabilized by CCN (left), BCN (middle), and ClaCN (right). Reproduced with permission from ref 45. Copyright 2012 Royal Society of Chemistry. (c) A generic visualization of emulsion formulation showing the interplay between formulation and composition variables, leading to different emulsion morphologies, including double or multiple emulsions (see text).

The interfacial properties of nanocelluloses with various shapes and surface chemistries, produced by acid hydrolysis of eucalyptus fibers (CNCa) and enzymatic hydrolysis of bacterial cellulose (CNCe), respectively, were compared to reveal their surface activity and ability to form Pickering systems.[70] Compared to CNCa, CNCe showed a larger affinity for hydrophobic surfaces. The possible presence of surface-bound proteins (residual cellulolytic enzymes) may partially explain this observation along with the distinctive surface roughness that was proposed to be of major impact on the ability of CNCe to stabilize sunflower oil/water interfaces. These results give rise to the fact that the interfacial behavior, and thus the applications of CNC, can be tuned by controlling its surface properties and shape.

Emulsions and Nanocellulose−Surfactant Interactions. Given the inherent, nonamphiphilic nature of nanocelluloses, efforts have been devoted to impart improved interfacial adsorption.[71] Among them, facile surface modification helps to engineer the properties of nanocelluloses and to tune their behavior at the oil/water interface.[8] The effect of nanocelluloses, when used as a component of surfactant-stabilized emulsions, favors systems with water as the continuous phase. In practice, this means that emulsion inversion from oil-in-water (O/W) to water-in-oil (W/O) is prevented; see Figure 3c for a map illustrating the possible emulsion morphologies, depending on the composition and formulation variables. More specifically, observations as far as the effect of nanocelluloses in surfactant-stabilized emulsions indicate that the presence of cellulosic nanoparticles is akin to the effect of a viscosifying additive that displaces the transitional inversion line. For example, the presence of nanocelluloses limits

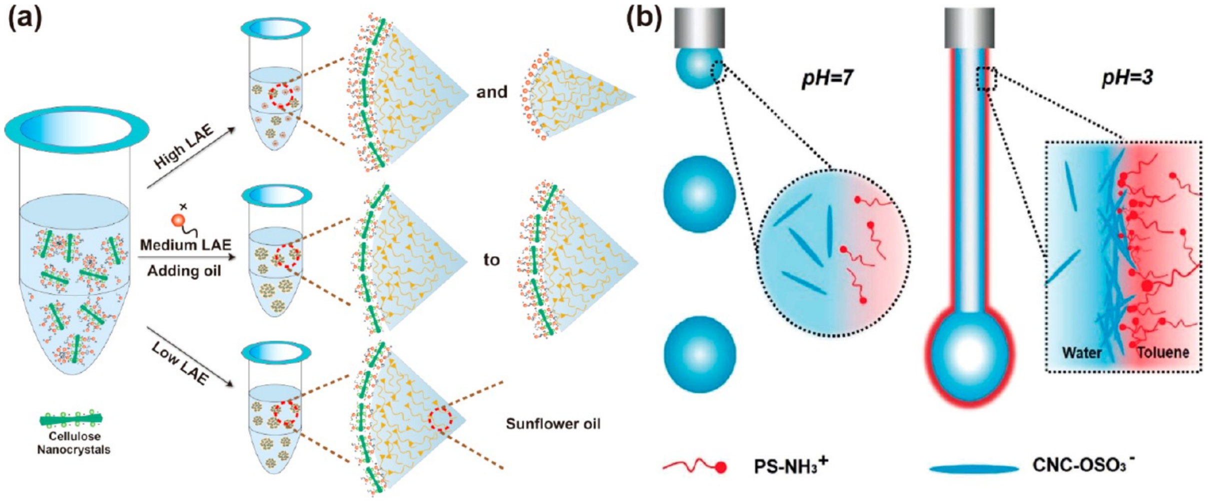

Figure 4. (a) Schematic illustration showing the interfacial behavior of CNC/LAE complexes at the sunflower oil/water interface. Adapted from ref 73. Copyright 2018 American Chemical Society. (b) Structuring of a liquid jet in tubular shapes through the rapid assembly of CNC/amine end-functionalized polystyrene nanoparticle-surfactants at the toluene/water interface. Adapted with permission from ref 74. Copyright 2017 Wiley-VCH.

emulsion inversion from O/W type to W/O type, as is normally done by changing a formulation variable, for instance, by increasing the salt concentration in emulsions stabilized by ionic surfactants. This is equivalent to moving the inversion boundary upward, as illustrated. Moreover, if the formulation variables are selected in such a way to produce oil-continuous systems in the absence of nanocelluloses (W/O emulsions, for example, if the formulation favors interactions with the hydrophobic phase), the addition of nanocellulose makes more likely the persistence of drop-in-drop or multiple emulsions of the water-in-oil-in-water (w/O/W) type. In effect, this is qualitatively equivalent to a shift to the left in the position of the catastrophic inversion line of Figure 3c. Note that the changes in the transition boundaries described here are to be taken only as illustrations to rationalize the effect of nanocelluloses because, to our knowledge, such phenomena have not been shown experimentally.

The transition behavior has been studied in the presence of a cationic surfactant that electrostatically modified the surface properties of CNC.[72] The results indicated that the interactions between anionic CNC and cationic alkylammonium surfactants (dodecyl dimethylammonium bromide (DMAB) and cetyltrimethylammonium bromide (CTAB)) significantly affected the interfacial behavior of CNC. Specifically, aggregation of surfactant molecules on CNC occurred when the concentration of surfactant exceeded the apparent critical micelle concentration (cmc),[73] which dramatically increased the hydrophobicity of CNC and enabled better wettability at the oil/water interface. By adsorbing cationic DMAB, which contains two alkyl tails, a double transitional change was observed, from enhanced interfacial bending for CNC toward dodecane at low DMAB concentration (O/W, Figure 3c), over curvature reversal to achieve interfacial bending toward water at intermediate DMAB levels (W/O, Figure 3c), to return to the oil-in-water form at higher DMAB loading (O/W, Figure 3c).

Recently, we used a food-grade cationic surfactant, ethyl lauroyl arginate (LAE), to engineer the behavior of CNC at the sunflower oil/water interface.[73] The adsorption of CNC at the interface was studied as a function of LAE concentration (Figure 4a): three interfacial adsorption regimes at given surfactant loading were observed, depending on its structure adsorbed on CNC, as unimer or as adsorbed admicelles. For instance, at low LAE addition, the emulsion droplets were stabilized by complexes containing partially neutralized CNC. At medium LAE concentration, the system underwent a transition from nearly neutralized CNC aggregates to CNC aggregates containing adsorbed LAE bilayers or admicelles. At high LAE concentration, the oil droplets were stabilized by both the complexes containing fully covering CNCs and by LAE molecules. Finally, the oil phase type influenced the interfacial behavior of CNC. Both, CNC/LAE complexes and LAE molecules contributed to stabilize viscous, nonpolar sunflower oil. In contrast, when a less viscous oil was used, only LAE adsorbed at the interface, and CNCs were preferably located in the bulk of the aqueous phase.[72] The results demonstrate a promising opportunity to controllably tune the interfacial adsorption of CNC by introducing a cationic surfactant, depending on the oil composition.

Besides the surface engineering of CNC by adsorbing oppositely charged surfactants, a more sophisticated but useful approach is to apply nanoparticle−surfactant systems (NPS) in situ.[74] CNC-based NPS were generated at the toluene/water interface via electrostatic interactions between charged groups of CNC and amine end-functionalized polystyrene originally dispersed in toluene. Structured liquids, generated by interfacial effects, assembly, and jamming of NPS took place, forming a robust barrier with exceptional mechanical properties (Figure 4b). The pH-switchability of amine groups enabled a controlled response of the CNC-based NPS. Taking advantage of these effects, a jet of CNC aqueous suspension free-falling into a toluene solution produced aqueous tubules (stabilized when the CNC-surfactants were jammed at the interface).

CNC and CNF Synergies in Pickering Emulsions. From green and sustainable perspectives, there is a need to develop facile, efficient methods to control the behavior of nanocelluloses at the oil/water interface. The combination of the two types of nanocelluloses to exploit their synergies is a highly attractive alternative. Recently, we investigated a system that included both CNC and CNF in a single stabilization step.[75] CNC primarily stabilized the (sunflower) oil/water interface, via adsorption. Moreover, at given amounts of non-adsorbing CNF, depletion effects developed, which changed the aggregation state of the oil droplets, via either depletion flocculation or

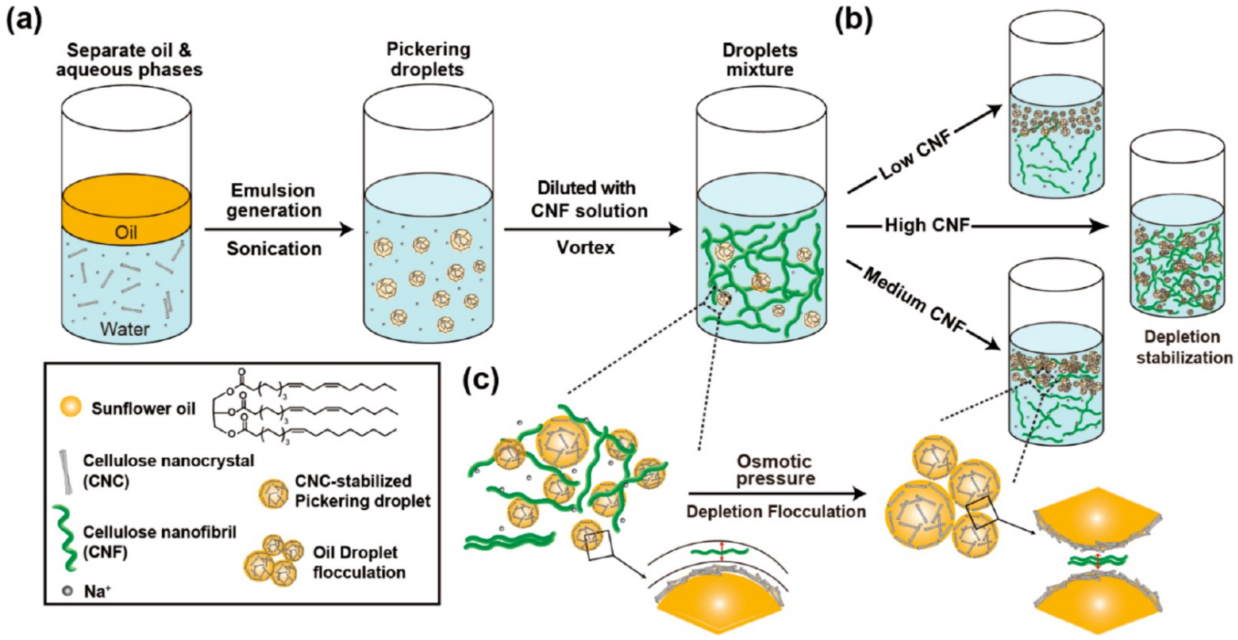

Figure 5. Schematic illustration of (a) emulsification process toward stable CNC-based Pickering emulsions followed by addition of CNF. (b) Three stabilization regimes were induced, depending on CNF concentrations. (c) Depletion flocculation of oil droplets in the CNC-stabilized Pickering emulsions was observed with nonadsorbed CNF reaching the critical flocculation concentration. Adapted with permission from ref 75. Copyright 2018 Royal Society of Chemistry.

depletion stabilization (Figure 5a). At low CNF concentration, creaming of the oil droplets occurred because of the difference of density of the phases. At intermediate CNF concentration, significant flocculation occurred, induced by osmotic effects between droplets in the presence of CNF (Figure 5c). Upon further increasing of the concentration of CNF, depletion stabilization took place (Figure 5b). It should be noted that the oil/water interface stabilized by CNCs was intact and no droplet coalescence was observed, owing to the formed, mechanically robust interfacial layers. The results form the basis of an approach that uses non-adsorbing CNF to control the interfacial and bulk behavior of CNC-stabilized emulsions.

Colloidal Lignin at the Oil/Water Interface. The phenylpropane monolignols (p-hydroxyphenyl, guaiacyl, and syringyl) of lignins are linked to form complex, 3D-branched structures possessing a hydrophobic backbone and hydrophilic side chains that effectively reduce the surface tension of water.[76,77] This ability of lignins has been noted to depend on the molecular weight, types of functional groups, and solubility. The behavior of lignins at the oil/water interface, however, is different from that of most conventional synthetic surfactants. High concentrations, from 1 to 10%, are needed to effectively lower the surface tension, and instead of undergoing micellization at the cmc, associative structures are formed by lignins. Lignin stabilizes emulsions by adsorption at the oil/water interface, which prevents droplet coalescence by electrostatic and steric repulsion (Figure 6a).[77] Importantly, the possible presence of residual molecules cannot be ignored, such as extractives and carbohydrates (as in lignin-carbohydrate complexes), which even if present in very small amounts affect the overall surface activity of the "lignins".[78]

In earlier work, lignins were separated according to their molecular weight from spent pulping liquors by acid precipitation and ultrafiltration.[76] They were tested according to their capacity to reduce surface tension when dissolved in aqueous solutions.[79] The results showed that higher molecular weight lignins were more surface active. Sjöblom et al. studied the effect of molecular weight of lignosulfonates on the stability of O/W emulsions with a light petroleum (C9−C16) distillate.[80] They concluded that lignins adsorbed at interfaces and promoted flocculation by bridging adjacent droplets; higher molecular weight fractions of lignin resulted in enhanced stability.

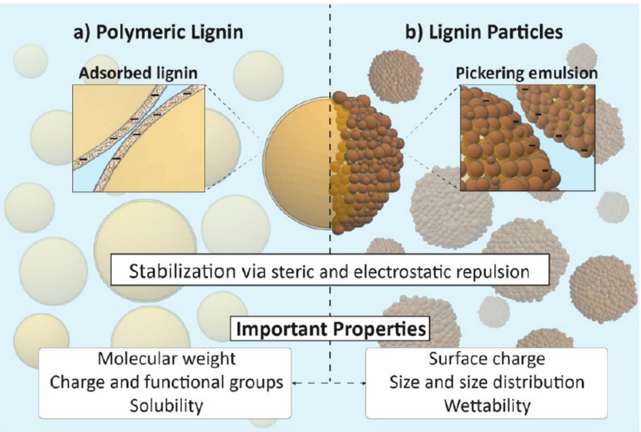

Figure 6. Lignin at the oil/water interface. Mechanisms and properties affecting the behavior of lignins at the oil/water interface as (a) macromolecular colloids and (b) as particles. In panel a, associated molecules display interfacial activity and stabilize the oil/water interface by adsorption of such structures. In panel b, the colloidal particles adsorb via typical Pickering stabilization.

Functional groups, carbonyls, carboxyls, and aliphatic-hydroxyls present in the structure of lignins, play important roles in the hydrophilic−lipophilic balance. Similar to the monolignols, functional groups exist on the lignin, depending on the lignin, depending in its source and, together with molecular weight, can vary according to the extraction processes. For instance, coming from the sulfite pulping process, lignosulfo-

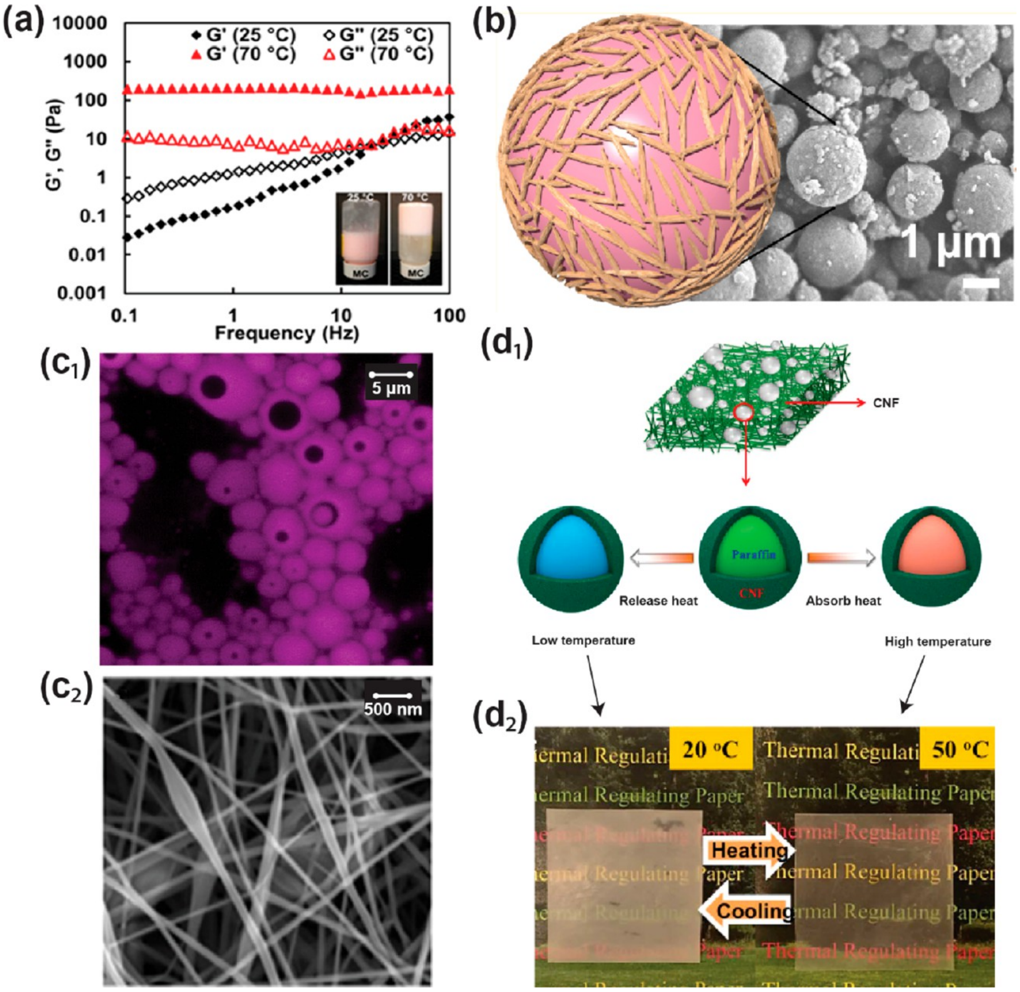

Figure 7. Applications of nanocelluloses adsorbed at the oil/water interface. (a) Storage and loss modulus of CNC-hydroxyethyl cellulose emulsion with added methyl cellulose indicating gel formation at 70 °C. Reproduced from ref 87. Copyright 2015 American Chemical Society. (b) CNCs and surfactant as costabilizer for poly(methyl methacrylate) (PMMA) latex. Reproduced from ref 88. Copyright 2017 American Chemical Society. (c_1) Confocal fluorescence microscopy image of an emulsion containing CNF in aqueous phase and polystyrene (PS) in toluene at 90/10 PS/CNF dry mass ratio. (c_2) Electrospun nanofiber web from the emulsion in panel c_1. Adapted with permission from ref 92. Copyright 2016 Royal Society of Chemistry. (d_1) Encapsulation of paraffin by CNF for formation of thermal regulation composites. (d_2) Phase change material paper structures during heating–cooling cycles. Adapted with permission from ref 93. Copyright 2017 Elsevier.

nates contain considerable amounts of sulfite and hydrogen sulfite ions, which make this lignin water-soluble at neutral pH.[80] Kraft lignins, presenting lower levels of sulfur and being by far the most widely available, have also attracted attention, but they may require chemical modification (e.g., carboxymethylation or acetylation) for changing their solubility and surface activity at neutral pH.[77,81,82]

Colloidal Lignin Particles. Recently, spherical lignin particles have been proposed as promising alternatives to stabilize Pickering emulsions (Figures 1e and 6b). Such particles can be generated by several methods, including aerosol drying, precipitation with acid, ultrasonic irradiation, mechanical homogenization, antisolvent exchange, and emulsion inversion, among others.[14] In one of our previous studies,[46] a method for producing lignin particles via aerosol flow was introduced, and particles with different hydrophilicity (originating from Kraft and Organosolv lignins) were used to formulate Pickering emulsions. Briefly, a lignin solution was atomized and subsequently dried during flow through a heated laminar flow. With this method, dry particles with sizes ranging between ca. 30 nm and 2 μm could be produced and fractionated by size. Oil-in-water Pickering emulsions were prepared, and their stability was shown to depend on particle size, concentration, and surface energy. More specifically, more stable emulsions were obtained using Kraft lignin particles with the smallest average particle diameter, ~0.4 μm, at the highest concentration used, 0.6% w/v in water. This was somewhat unexpected because it is known that the barrier for desorption of particle-stabilized emulsions increases with the particle size, as was shown in related systems.[83] One can speculate that one reason for the higher stability observed with the smaller lignin particles may be related to the size polydispersity and number density.

When considering lignin type, compared to Kraft lignins, those from the Organosolv process display an enhanced hydrophobicity and lower interfacial affinity. The surface characteristics of lignin particles (chemical composition, wettability, and electrostatic charge), which can be tuned readily (from its origins or depending on the source as well as isolation methods and possible postmodification), makes them ideal for interfacial modification and for tailoring their behavior at a given oil/water interface.

EMULSIONS AND APPLICATIONS

Emulsions Based on Nanocelluloses. The capability of nanocelluloses to stabilize an emulsion depends on many variables, such as source, aspect ratio, and surface charge, among others. Because of the natural hydrophilic character of cellulosic nanomaterials, most efforts in this field have focused on O/W emulsions. However, W/O or double emulsions can also be formed by chemically modified nanocelluloses, via hydrophobization or surfactant complexation (Figure 3c). As described before, compared to common particle stabilizers, the advantages of cellulose nanoparticles include their biocompatibility, biodegradability, low density, and low cost.

Kalashnikova et al. have demonstrated highly stable emulsions with unmodified CNC isolated from cotton, green algae, and bacterial cellulose (Figure 3a,b).[45,63] The possibility of producing functional emulsions with modified CNC was also demonstrated.[73,84] We prepared thermoresponsive O/W emulsions with CNC grafted with *N*-isopropylacrylamide (NIPAM), namely, CNC-*graft*-poly(NIPAM).[71] The CNC-*graft*-poly(NIPAM) aligned and layered at the oil/water interface, which contributed to the stability during a four-month observation time. When the emulsions were heated above the lower critical solution temperature of poly(NIPAM), the emulsions broke down. The demonstrated production of emulsions with controllable stability using naturally abundant resources is potentially useful for biomedical and cosmetic applications. Low et al. prepared dual responsive (pH and magnetic) emulsions using Fe_3O_4−CNC composites for stabilization.[85] The fabricated emulsions were proposed for application as smart nanotherapeutic carriers. Ojala et al. studied the stabilization of marine diesel O/W emulsions with bifunctionalized CNC for application as oil-spill response agents.[86] Apart from chemical modification of CNC, Pickering emulsions have also been produced via synergistic stabilization by CNC and water-soluble polymers (e.g., hydroxyethyl cellulose (HEC) and methyl cellulose (MC)). By adding MC to CNC-HEC stabilized emulsions, followed by heating above 70 °C, viscoelastic emulsion gels were achieved (Figure 7a).[87] The emulsion gels were stable within multiple cycles of heating−cooling. Kedzior et al. exploited a synergistic effect between CNC and surfactants for miniemulsion polymerization (Figure 7b).[88] The resulting latexes showed tunable properties (morphology, surface charge, and molecular weight), which bear potential applications for coatings, adhesives, and household products. Tasset et al. used CNC-stabilized O/W emulsions for the preparation of highly porous foams.[89] The preparation of composite foams was demonstrated by the addition of chitosan to the corresponding emulsions.

In addition to modifying nanocelluloses for emulsion stabilization, increasing the viscosity of the continuous phase is also of interest. Because of the long fibrillar structure and high aspect ratio of CNF, they can be effective in the stabilization by their effect on the continuous phase.[75] The addition of surfactant is also useful in tailoring the properties of the emulsion. For example, we showed that the morphology, viscosity, and stability of emulsions can be tuned, depending on the concentration of CNF and sodium dodecyl sulfate.[90] When the CNF content was increased, the viscosity of the continuous phase was enhanced, the droplet size reduced, and emulsion stability improved.[91] We used a nonionic surfactant to compatibilize CNF with polystyrene (PS) in w/O/W double emulsions (see also Figure 3c).[92] The emulsion was a drop-in-drop of the w/O/W type, as shown in Figure 7c_1 with the aqueous phase shown in black and the oil phase in color. Such a system makes it possible to compatibilize phases with different polarity and, upon removal of the solvents, to produce composite polymeric structures with high interfacial areas, which is appealing for numerous applications. Because of the shear thinning behavior of double emulsions containing CNF and PS, electrospun nanofibers could be fabricated from such precursors (Figure 7c_2). CNF has also been used to encapsulate paraffin in the form of a Pickering emulsion, which can be consolidated into a phase change material, as a paper structure for solar energy applications (Figure 7d).[93]

In the case of W/O emulsions, surface modification is critical for emulsion stabilization, e.g., by affecting the wettability of the cellulosic particles.[84] Lif et al. studied water-in-diesel emulsions using nonionic surfactants, sorbitan monolaurate, and glycerol monooleate as emulsifiers and hydrophilic or hydrophobic CNF as a stabilizer.[94] The motivation for producing water-in-diesel emulsions was to improve the emission profile in combustion compared to regular diesel. For hydrophobization, CNF was treated with octadecylamine or poly(styrene-*co*-maleic anhydride), given that silylation was not suitable for fuel applications (silicon poisons the exhaust catalyst). It was concluded that both the surfactant and the stabilizer were needed to produce reasonably stable emulsions. The most stable emulsions were obtained by combining hydrophobic and hydrophilic (unmodified) CNF. Cunha et al. hydrophobized CNF and CNC with lauroyl chloride, which stabilized W/O and o/W/O double emulsions.[95] In the double emulsions, unmodified nanocelluloses were used to stabilize the inner, oil/water interface, while the modified nanocelluloses stabilized the outer, water/oil interface.

Food Emulsions. Because O/W emulsions are an integral part of pharmaceutical, foodstuff, and cosmetic formulations, either during production or in final product forms, there is an increased demand for label-friendly products fabricated from natural and renewable ingredients.[96] Health and safety issues have been considered in attempts to replace conventional synthetic surfactants with nanocelluloses and lignin.[97] Research on food emulsions stabilized by particles has mainly focused on fat crystals, inorganic particles, protein-based nanoparticles and chitin nanocrystals, used as stabilizers. Few efforts using nanocellulosic particles in food-grade emulsion systems have been reported.[73,98−101] It is interesting to note that Turbak et al., who pioneered work on nano/microfibrillar cellulose, first considered their use as food additives.[102] Lignin and nanocelluloses for food have been limited by uncertainty in their availability, regulation, and cost structure, but this situation may change rapidly, with the prospects of several commercial units opening production.[12]

Golchoobi et al. studied combinations of CNF, guar gum, and CMC in low-fat mayonnaise, an O/W emulsion.[100] The combination of CNF and guar showed better stability compared to a commercial control sample. CNF was reported to have a positive effect on the mouthfeel of the mayonnaise. Mikulcová et al. studied the encapsulation of essential oils (cinnamaldehyde, eugenol, and limonene) with carboxylated CNC and CNF to produce emulsions with antibacterial properties against typical food-borne pathogens.[101] According to their results, the droplet size of CNC-stabilized emulsions was smaller compared to CNF-stabilized emulsions. CNF-based emulsions were reported to be stable during a two-month storage without creaming,

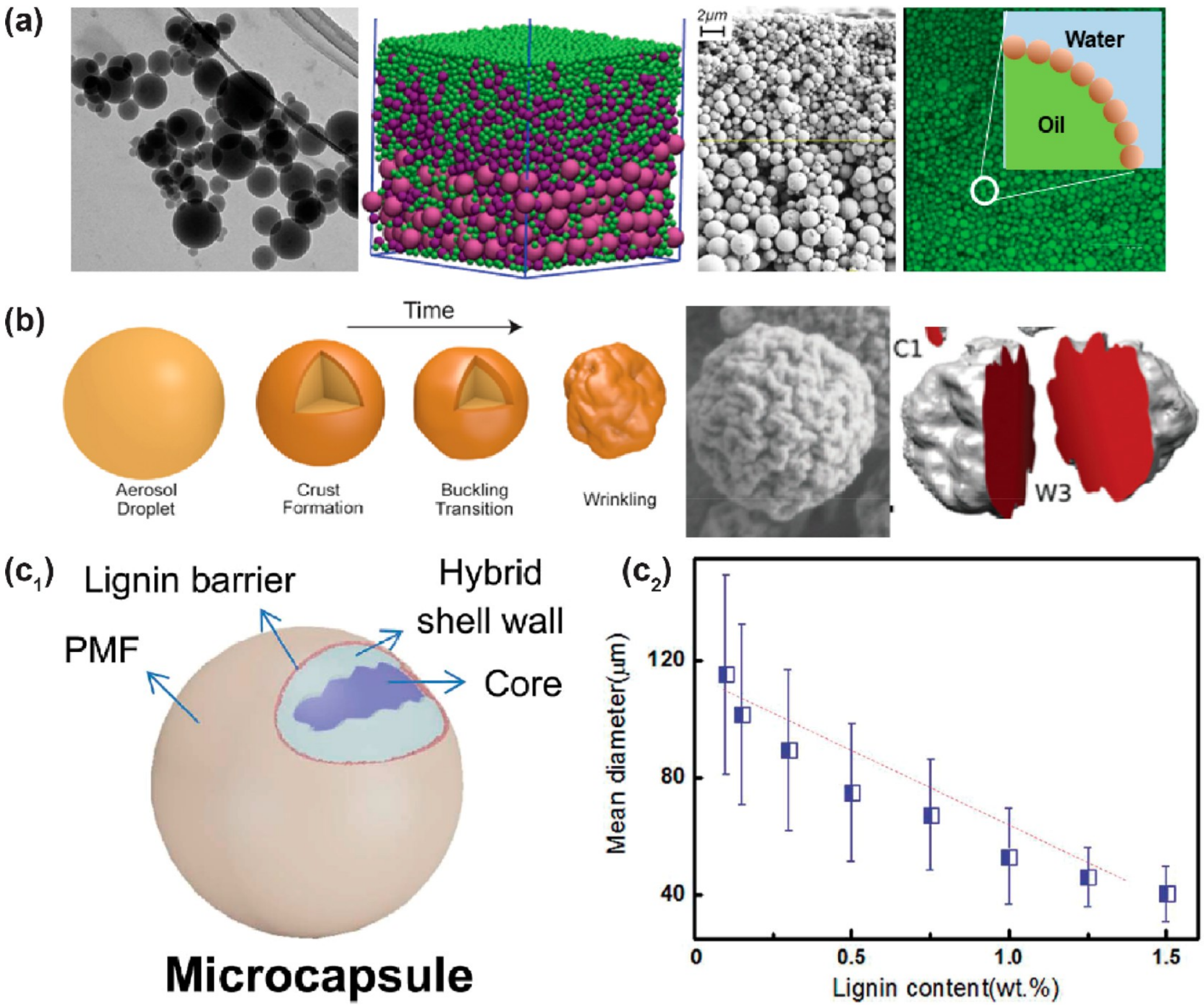

Figure 8. Applications of lignin particles at the oil/water interface. (a) Left: Transmission electron microscopy image of colloidal lignin particles obtained by aerosol flow technique. Middle: Modeling and SEM image of lignin particles forming a particulate film upon evaporation. Right: Fluorescent image of oil droplets stabilized by autofluorescent lignin particles. Adapted from ref 46. Copyright 2016 American Chemical Society. (b) Formation of wrinkled lignin particles during an aerosol flow process. Middle and right: SEM image and electron tomogram of lignin particles with wrinkling morphology. Adapted with permission from ref 109. Copyright 2018 Royal Society of Chemistry. (c1) Microcapsule prepared via lignin nanoparticle-stabilized Pickering emulsion template. (c2) Decrease in the mean diameter of the microcapsules with increasing lignin content in the Pickering emulsion template. Adapted with permission from ref 110. Copyright 2015 Royal Society of Chemistry.

which was attributed to a formation of a strong fibril-droplet network due to the high aspect ratio of CNF.[75]

Safety and regulatory issues need to be fully addressed.[54] For nanomaterials, it is not possible to evaluate the impacts on humans and the environment based only on the chemical characteristics.[55] Toxicity studies with nanocelluloses on mouse and human macrophages have been conducted by Vartiainen et al., who suggested that CNF prepared from friction grinding is not cytotoxic.[103] Pitkänen et al. found that CNF did not present genotoxicity or sublethal effects in in vitro tests but concluded that additional studies are needed to exclude possible genotoxic activity.[104]

Polymeric and Particulate Lignin, Coatings, and Emulsions. Applications of lignin include those related to fillers, binders, dispersants, or polymeric surfactants, and only around 5% of over 70 million ton annual production of lignin is used for commercial applications.[105] The potential use of lignin for coatings and stabilizer of emulsions has been demonstrated,[77,81,82] while colloidal lignin particles have been used for coatings,[106] for loading of active compounds, as a template for functional polymeric capsules,[52] or for Pickering emulsions.[46] The surface activity of lignin is an attractive property that benefits the stabilization of multiphase systems, including Pickering templates for microcapsules and nanoparticles, organic carriers for inorganic particles, emulsion with gas-switchable features, and tunable emulsion, among others. Our proposed aerosol flow system for high-throughput and high-yield production of lignin nano- and microparticles is relevant because of the tunable size, hydrophilicity, and various surface morphologies that can be achieved (Figure 8a, left).[46] Such lignin particles comprising given sizes have been studied as far as their evaporation-induced self-assembly, to form particulate coatings with segregated structures, which were also followed by modeling (Figure 8a, middle frames).[106] The effect on emulsion stability of lignin particle size and concentration in the aqueous phase was studied in surfactant-free emulsification.[46] An

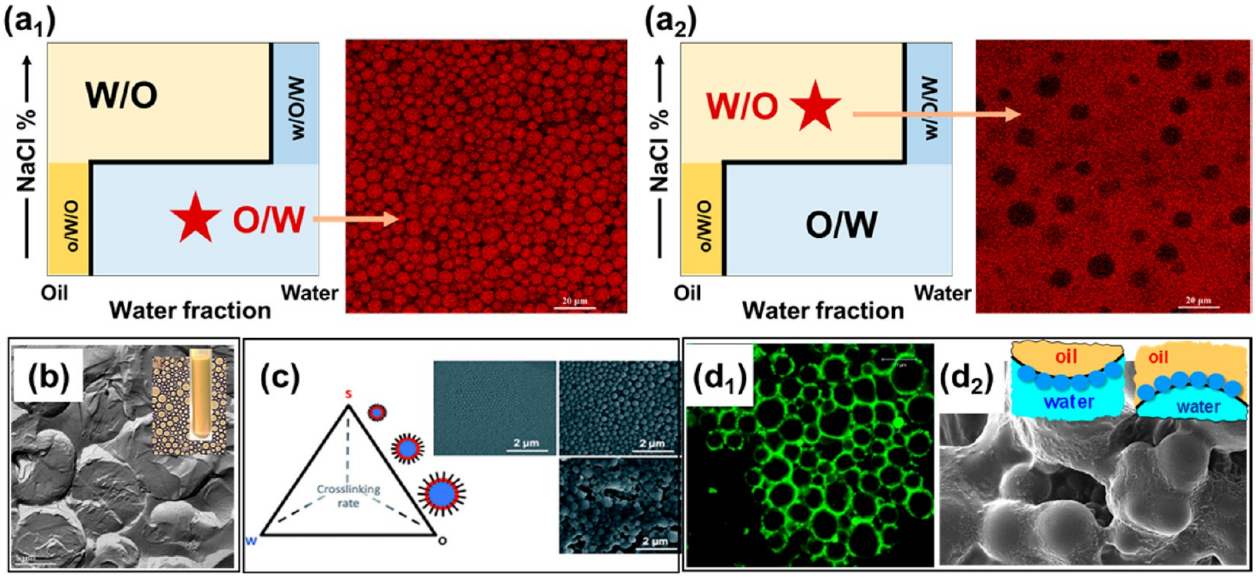

Figure 9. (a) Schematic representation of an anionic surfactant/oil/water (SOW) system containing CNFs. (a$_1$) O/W or (a$_2$) inverted W/O emulsions are formed by tuning the salinity (wt %) and CNF concentration. Adapted from ref 90. Copyright 2017 American Chemical Society. (b) O/W emulsions with oils of different viscosities stabilized by dissolved, modified lignin (see cryo-TEM of emulsified oil drops). Adapted with permission from refs 81 and 82. Copyright 2016 Wiley-VCH and Elsevier, respectively. (c) Lignin particles with uniform size synthesized from lignin solutions by surfactant-stabilized W/O emulsions. Adapted with permission from ref 83. Copyright 2015 Royal Society of Chemistry. (d) Fluorescent and SEM images of oil droplets surrounded by lignin particles obtained from emulsion precursors (see panel c) or from the aerosol flow method. Adapted from ref 46. Copyright 2016 American Chemical Society.

example was kerosene-in-water emulsions that were obtained by using given concentrations (0.1−0.6%) of Kraft lignin particles with varied average size (from ~350 to 1000 nm). An illustration of the adsorbed particles at the oil/water interface is included in Figure 8a, right. We also synthesized lignin supracolloids from W/O microemulsions and found them effective for the stabilization of Pickering emulsions.[83]

Surface roughness is a key factor for tuning the interfacial properties of colloidal particles, given the effective increase of overall surface area of the particles. It also has a consequence on the contact angle that influences particle adsorption behavior at interfaces[107] and the macroscopic properties and applications of particle-based systems. Particle wrinkling is a commonly occurring natural phenomenon.[108] In our recent efforts, wrinkling and other surface morphologies of colloidal lignin particles produced from the aerosol method were investigated by harmonic analyses.[46,109] It was shown that different morphologies were related to the onset of buckling transition during the drying phase of the aerosol flow synthesis. Such changes were time-dependent, going from spherical droplets, over crust and buckling formation, to final structures exhibiting wrinkling and crumpling (Figure 8b). Wrinkled lignin particles showed a similar surface roughness spectrum, wherein differences were found most noticeable in the large-wavelength region. The results are useful in efforts to design particles with tunable interfacial behavior and wettability. Furthermore, they provide a means to improve our understanding of the role of surface topography on colloidal interactions. Finally, incorporating corrugated surface features in plant-based colloids might offer an avenue for effectively utilizing, modifying, and extending their properties.

Microcapsules with different properties for utilization in various applications can be made via Pickering emulsion templates stabilized by lignin particles. Yi et al. successfully utilized lignin nanoparticles as a barrier to obtain a multilayer composite microcapsule via a Pickering emulsion template accompanied by in situ interfacial polymerization of a melamine formadehyde prepolymer (PMF) (Figure 8c$_1$).[110] Furthermore, the mean diameter of fabricated microcapsules decreased with increasing lignin content (Figure 8c$_2$), demonstrating the ability of lignin particles to control the properties of a Pickering system. Isophorone diisocyanate (IPDI) was richly and efficiently loaded into a lignin nanoparticle-based Pickering emulsion to produce a self-healing composite. IPDI reacted with water and moisture to form a solid. Thus, IPDI-loaded microcapsules were incorporated into epoxy coatings, and their anticorrosion effect was demonstrated on a steel plate (subjected to accelerated corrosion tests by immersion in a brine solution).

Tunable Pickering emulsions stabilized by lignin nanoparticles were achieved by grafting polyacrylamide on their surfaces.[111] The emulsion properties were influenced by salinity and grafting density, given that they affect lignin aggregation. Thus, emulsions with a wide range of properties could be produced. The development of gas-switchable Pickering emulsions stabilized by 2-(diethylamino)ethyl methacrylate (DEAEMA)-modified lignin particles was reported by Qian et al.[112] The CO_2/N_2 switchability of the modified lignin particles were finely tuned by the DEAEMA graft density and chain length. The demulsification/re-emulsification process of Pickering emulsions was achieved by alternating CO_2 and N_2 bubbling.

Lignin has also attracted interest in the biomedical field because of its biodegradability, biocompatibility, and low toxicity.[113] Of relevance are its antioxidant and antibacterial properties. The latter case was demonstrated by Velev et al.[114] The development of nanostructured lignin has led to potential uses in drug/gene delivery and tissue engineering.[115] However, there is limited knowledge on the toxicity of nanostructured lignin to humans. Lignin nanoparticles were used for drug delivery applications, and a low cytotoxicity of pure nanoparticles and iron(III)-complexed and Fe_3O_4-infused particles was reported.[113] The particles were also indicated to have good stability, were able to load hydrophobic drugs, and sustain their release.

■ INTEGRATION OF CELLULOSIC AND LIGNIN COLLOIDS

It is reasonable to discuss nanocelluloses or lignin particles together because they are both sourced from plant biomass, where they are the main components. They also form stable colloidal systems in aqueous suspension. However, there is perhaps a more compelling motivation: nanocelluloses carrying residual lignin exhibit properties that make them unique. Such synergies have been studied to a very limited extent. In addition, the integration of lignin (as lignin particles) with nanocelluloses can become quite attractive if one reflects on recent developments that exploit the strong interactions between these two components. This goes from ultrastrong wood panels that are obtained upon densification of cellulosic fibers in the presence of lignin[116] to the very strong and flexible nanocomposites produced by mixing modified CNF and an industrial lignin.[117] In fact, earlier we introduced the subject when researching the role of residual lignin in films or nanopapers comprising "ligno-nanocellulose" (see refs 21 and 22 and references therein). The question remains whether similar compositions are effective in stabilizing fluid/fluid interfaces. This is yet to be determined but is a topic currently under our consideration. In retrospect, such possibilities are not surprising if one reflects on the role of cellulose and lignin in the cell wall of plants. Therein, strong interactions and synergies are part of a multifunctional and hierarchical structure that responds efficiently to several demands.

■ PROSPECTS AND CONCLUSIONS

Progress on lignin and nanocellulose applications is accelerating rapidly. This includes uses as rheology modifiers, in coatings and stabilization of multiphase systems,[75] in liquid crystals,[42] in hybrid materials,[118] and as templates for functional materials,[52] among many others. A recent development in our group was the construction of nanocellulose-based customizable, three-dimensional structures. This was accomplished by a biofabrication technique that relied on hydrophobic particles that prestabilized the air/water interface and resulted in a robust network of cellulose fibrils synthesized by bacteria.[119] As a starting point for related developments, the use of emulsions can be quite attractive. Figure 9, for example, illustrates the different possibilities, which include O/W or W/O emulsions in the presence of CNF (Figure 9a) or solubilized lignins in the stabilization of O/W emulsions (Figure 9b). Such systems can be useful in the design of advanced materials. One of the routes for lignin particle fabrication has been introduced before (aerosol flow method). If a control in the lignin particle size is wanted, emulsions can be used to produce such uniform lignin particles, which can be further crosslinked (Figure 9c). In turn, they can also be used in the stabilization of emulsions (Figure 9d). The multiphase systems that are presented here, based on nanocelluloses or lignins, are ideal for the fabrication of microbeads, hollow microcapsules, and magneto-responsive hybrid materials.[120]

Considering previous sections on stabilization of oil/water interfaces, any application makes the adjustment of the supramolecular interactions imperative to separate and disperse the nanocelluloses. Grafting polymers opens ample possibilities to alter the hydrophobicity for self-assembly and, importantly in the present context, to incorporate supramolecular moieties to tune the organization and properties at the oil/water interface.

Lignocellulose as a renewable feedstock makes a good case to respond to the demands for sustainable use of natural resources and environmental consciousness. Moreover, there is an interest in exploiting lignocellulose's unique functionalities. Specifically, in the colloidal forms (here nanocelluloses and lignin particles), they combine their intrinsic features and their characteristic shapes and sizes toward a large variety of promising performances. Triggered by their fascinating properties, especially the distinctive interfacial behavior, advanced applications of ligno-nanocellulose at the oil/water interface will develop extensively and profoundly, evolving from fundamental insights to practical aspects. The inherent ability of ligno-nanocellulose to self-assemble at the oil/water interface facilitates supra-structures and highly hierarchical assemblies. They also allow functional products because of the strong interfacial reinforcement effect, presenting potential advantages in the fields of drug delivery, personal care, porous material, etc.

Further understanding and unveiling the dynamic partitioning and assembly behavior of ligno-nanocellulose at the oil/water interface, related to the interfacial free energy during and/or after adsorption, remains challenging. Modifications of ligno-nanocellulose can bridge the gap between bulk properties and unique product functions; however, the modification always leads to alterations of physicochemical properties, which is undesirable for green resources. As for the toxicity of modified ligno-nanocelluloses, efforts should be devoted to maintaining its biocompatibility while achieving the expected performance. Furthermore, although ligno-nanocellulose has been commercially used in the biobased field, developing facile, efficient, and green technologies for production and postprocessing should be considered.

Research on the dynamic behavior of plant-based colloids at interfaces is of great interest. They can reduce the need for synthetic materials used in colloid systems and will open new opportunities for revealing novel functional applications of structurally defined natural nano- and microparticles. We leave this feature article with some questions that were partially addressed but remain open for discussion: What factors affect the assembly of plant-based colloids at the oil/water interface? What are the dynamics of nanocelluloses and lignin particles adsorbed at the interfaces? What applications and properties are possible as a result of the stabilization of fluid/fluid interfaces, in the form of emulsions with given morphologies? How can nanocelluloses and lignin particles be combined to develop yet new compositions that exploit their interesting synergies? Are there other plant-based colloidal materials that should be considered, for example, heteropolysaccharides, proteins, and extractives?

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Ph.D. student **Luiz G. Greca** was awarded an exchange scholarship from The Brazilian National Council for Scientific and Technological Development (CNPq). During this time, he enrolled in marine technology and materials science courses at Aalto University and worked for six months at the Technical Research Centre of Finland (VTT). In 2016, he graduated as a Mechanical Engineer at the Pontifical Catholic University of Paraná, Brazil. Currently, his research interest includes the fabrication of structured lignocellulosic materials for high-value applications.

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Postdoctoral fellow **Siqi Huan** obtained her M.Sc. and Ph.D. degrees in Wood Science and Technology from Northeast Forestry University, PR China in 2013 and 2016, respectively. Her current research interest focuses on applying 3D-printing methods to design and create nanocellulose-based functional materials, including inks based on plant-based emulsions.

Postdoctoral fellow **Robertus Wahyu N. Nugroho** received his Ph.D. in polymer science at KTH Royal Institute of Technology, Sweden, during which he focused on surface chemistry of biodegradable polymers aiming at 3D scaffold design using particulate materials. Currently, he is working on the colloidal and storage stability of infant milk powders in a collaborative project with Valio Ltd, a Finnish dairy company.

Postdoctoral fellow **Blaise L. Tardy** obtained his M.Sc. in bioengineering from the Swiss Federal Institute of Science and Technology (EPFL), Switzerland (2009) and his Ph.D. degree in Chemical and Biomolecular Engineering from The University of Melbourne, Australia (December 2015). His current research interests include the formation of structured materials from nano- and microparticles of lignins and cellulose with a focus on the formation of hierarchical (super)structures.

Professor Orlando Rojas is chair of the Materials Platform of Aalto University. He is the recipient of the 2018 Anselme Payen Award, one of the highest recognitions in the area of cellulose and renewable materials. He has been elected Fellow of the American Chemical Society and the Finnish Academy of Science and Letters and is the recipient of the 2015 Tappi Nanotechnology Award. His most recent project grant includes a European Research Commission Advanced Grant (ERC-Advanced). He has published over 350 peer-reviewed papers related to the core research of his group, Bio-based Colloids and Materials, which mainly deals with nanostructures from renewable materials and their utilization in multiphase systems. He is a PI of the Materials Bioeconomy Flagship and co-PI of the Academy of Finland's Center of Excellence in Molecular Engineering of Biosynthetic Hybrid Materials Research, HYBER (2014−2019).

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