

# Tailoring Nanostructured Cellulose for Efficient Pickering Emulsions Stabilization

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Nanostructured celluloses, nanofibrils (CNFs) and nanocrystals (CNCs), are prepared through TEMPO-mediated oxidation by controlling the intensity of the process modulated by catalyst concentration and processing time. These nanomaterials are evaluated as stabilizers for Pickering emulsions, fabricated using high-pressure homogenization (HPH). Both CNFs and CNCs exhibit efficient steric and electrostatic stabilization of oil-in-water (O/W) emulsions. CNFs display strong inter-droplet interactions, leading to the formation of a 3D fibrous network emulsion with higher viscosity compared to CNCs-stabilized emulsions. However, CNFs also show a higher tendency toward flocculation, due to fibrils' entanglement in the continuous phase. Interestingly, the HPH treatment has a notable impact on the CNFs' interfacial layer, enhancing the emulsifying ability of CNFs and improving stability against coalescence. Conversely, CNCs-stabilized emulsions exhibit lower viscosity but demonstrate higher interfacial activity and stabilization capability. Remarkably, no phase separation during 10 months of refrigerated storage, indicating excellent long-term stability. Importantly, the HPH treatment does not significantly change the emulsifying ability of CNCs. In conclusion, this study highlights the possibility of obtaining nanocelluloses (NCs) with tailored emulsifying properties by regulating the intensity of TEMPO-mediated oxidation applied to pulp cellulose. These findings open up new opportunities for the development of innovative ingredients for the food and cosmetic industries.

## 1. Introduction

Emulsion systems have undergone thorough investigation with respect to their complex interactions with product interfaces and other ingredients, alongside a comprehensive examination of stabilization issues.<sup>[1]</sup> These investigations have revealed a broad spectrum of applications across various industries, including agri-food, biomedical, petrochemistry, and environmental remediation. In recent years, there has been a shift in wards smaller scales, particularly microemulsions and nanoemulsions, characterized by droplet sizes <1  $\mu\text{m}$ . To stabilize these emulsions without relying on surfactants, there has been growing interest in utilizing particles as stabilizers at the oil–water interface.<sup>[2,3]</sup> Pickering emulsions, stabilized by particles, offer several advantages,<sup>[4]</sup> such as reduced environmental and health concerns and enhanced stability due to the nearly irreversible adsorption of the particles at the liquid interface,<sup>[5]</sup> where they form a compact and dense layer, leading to efficient steric repulsion.<sup>[6]</sup> These emulsions hold significant promise in the pharmaceutical and food industries for applications like drug delivery systems, nutraceutical vehicles,

edible films, and wastewater management.<sup>[7–10]</sup> However, despite the recognition of the vast potential of Pickering emulsions, their practical implementation requires further investigation. The characteristics of particles employed as stabilizers play a fundamental role<sup>[3]</sup> in their behavior at the oil-water interface, influencing self-assembling tendencies, interfacial particle layer thickness, and cohesion. In addition to the chemical composition and surface functional groups, physical parameters, such as size, shape, and crystallinity, impact the tuning of Pickering emulsion characteristics and performance according to the desired application.<sup>[11]</sup>

While numerous solid particle materials of both inorganic or organic origins have been employed,<sup>[12]</sup> recent interest has turned to nanoparticles from natural sources, as they offer the advantage of self-assembling driven by nanoscale forces<sup>[13]</sup> coupled with limited environmental impact and no toxicity concerns.<sup>[14]</sup> Within this context, various organic particles of natural origin have been explored, including biopolymers such as

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polysaccharides, lignin, and proteins, as well as microorganisms and molecular assemblies. However, it is noteworthy that only a few of these natural particles have demonstrated the capability to stabilize Pickering emulsions in their pristine state. In the majority of cases, a modification process was necessary to impart the required techno-functional properties for effective emulsion stabilization.<sup>[15]</sup> The need for such modifications underscores the importance of tailoring the particle characteristics to achieve optimal performance as Pickering emulsion stabilizers.

Cellulose-derived nanomaterials, known as NCs, have emerged as promising stabilizers due to their abundance, sustainability, environmental friendliness, and biocompatibility.<sup>[16,17]</sup> While NCs in pristine state, find use in films, hydrogels,<sup>[18]</sup> and emulsions<sup>[19]</sup> fabrication, chemical modifications and hybridizations with inorganic nanoparticles enhance their versatility for various applications.<sup>[20–24]</sup>

NCs exhibit good water dispersibility, leading to highly stable colloidal suspensions. Their amphiphilic nature arises from the exposure of crystalline faces with largely different polarity, making them particularly appealing for the stabilization of water-oil interfaces, such as for Pickering emulsion<sup>[25–27]</sup> and capillary suspensions.<sup>[28]</sup> Among different methods developed for obtaining NCs from various sources,<sup>[29]</sup> TEMPO-mediated oxidation stands out as the most versatile approach.<sup>[30]</sup> This method allows for the generation of NCs with diverse morphologies (NCs particles with 10–30 nm in diameter and 40–60 nm in length) by fine-tuning the reaction conditions.<sup>[31]</sup> The ability to control NCs' morphology through TEMPO-mediated oxidation makes it an indispensable tool for tailoring NCs' properties to suit specific applications, despite the high carbon emissions and generation of waste streams associated with the process.<sup>[32]</sup> Consequently, there is a growing interest in developing milder reaction conditions that can offer a more sustainable and eco-friendly alternative.<sup>[33]</sup>

Among NCs, CNFs and CNCs have drawn attention for their high and low aspect ratios, respectively. The diameter of CNFs is typically reported to be in the nanoscale, i.e.,  $\approx 1$ –100 nm and their length is typically up to a few micrometers. Conversely, CNCs' diameter and length are in the range of 2–25 nm and 100–750 nm, respectively.<sup>[34]</sup> These rather wide and overlapping ranges do not allow a clear distinction between CNCs and CNFs based on their size. Therefore, while previous research has mainly focused on their size-based distinction, recent trends base the classification on their unique structural properties, such as flexibility and stiffness, which play a crucial role in their emulsification behavior.<sup>[35]</sup> More specifically, CNCs are characterized by being stiffer and shorter rods, while CNFs are longer and more flexible, with kinks and splits leading to entanglement.<sup>[35]</sup> Moreover, exploring the structural variations of these nanomaterials while maintaining their similar chemical nature presents a fascinating opportunity. Numerous studies have explored correlations between NCs length,<sup>[36–38]</sup> preparation method, chemical modification,<sup>[39,40]</sup> and the strength and stability of emulsion structure and droplet size. These investigations have been the subject of recent reviews,<sup>[26]</sup> providing valuable insights into the relationship between NCs properties and their emulsification performance.

Despite the potential of NCs as Pickering emulsion stabilizers, systematic investigations into the fundamental aspects gov-

erning their stabilizing performance are limited.<sup>[41]</sup> This limitation is attributed to the vast number of experimental parameters that need consideration in NCs fabrication, hindering a comprehensive understanding of the correlation between NCs properties and emulsion characteristics. For example, in our recent study, we investigated the emulsification ability and emulsion stabilization capability of NCs derived from mechanical processing of pulp cellulose, using ball milling and HPH.<sup>[42]</sup> While the results showed promise regarding Pickering emulsion stabilization, the lack of precise control over the mechanical processes resulted in wide size distributions (with the 50th percentile of the cumulative size distribution of  $\approx 16$   $\mu\text{m}$  for ball milling and 22  $\mu\text{m}$  for HPH) and varying structures (amorphous for ball milling and defibrillated for HPH). As a consequence, drawing general conclusions regarding the relationship between NCs' structure and function in this context proved challenging.

Therefore, in this study, we address the challenge of advancing the understanding of the correlation between NCs structure and techno-functional properties related to emulsification, by employing the well-consolidated TEMPO-mediated oxidation, followed by ultrasound-assisted dispersion, to prepare NCs in the form of small and flexible fibrils (CNFs) and rod-like crystals (CNCs), with controlled morphology and surface charge. The objective is to establish a correlation between the physicochemical properties of CNFs and CNCs and the resulting Pickering emulsion properties ( $\zeta$ -potential, microstructure, and rheological properties) to enhance emulsion behavior and stability over time. By providing insights into the interplay between NCs characteristics and emulsion performance, our work contributes to advancing the utilization of NCs in various applications requiring stable emulsions.

## 2. Results and Discussion

### 2.1. Morphology and Interfacial Properties of NCs

Two types of NCs, CNCs and CNFs, obtained from different treatment conditions of the same cellulose raw material, were used as stabilizers for Pickering emulsions.

The morphological, topological, and size features of the as-prepared CNCs and CNFs were assessed using AFM. **Figure 1** displays representative images of CNCs and CNFs, with CNCs characterized by a needle-like structure, and CNFs by a fibrous network. Statistical analysis of CNCs' size, based on a data set of 900 CNCs images, individually resolved from AFM, indicated a length of  $170 \pm 90$  nm and a cross section of  $3.0 \pm 0.5$  nm. For CNFs, a comprehensive statistical analysis of size was challenging due to the entanglement propensity of the flexible and disordered regions within the fibers, as evident in the AFM images. However, an estimated average fiber cross section of 5 nm and a length  $> 1$   $\mu\text{m}$  were observed.

FT-IR spectroscopy was used to analyze the functional groups present in the NC samples. **Figure 2** illustrates representative spectra of CNCs (black trace) and CNFs (red trace). These spectra exhibit typical features characteristic of NCs. Specifically, notable peaks include the C–H rocking at  $910\text{ cm}^{-1}$ , C–O bond vibrations spanning in the range  $1030$ – $1100\text{ cm}^{-1}$ , the antisymmetric stretching vibration of the C–O–C glycosidic bond at  $1160\text{ cm}^{-1}$ , stretching vibration of the C–H bond at  $2900\text{ cm}^{-1}$

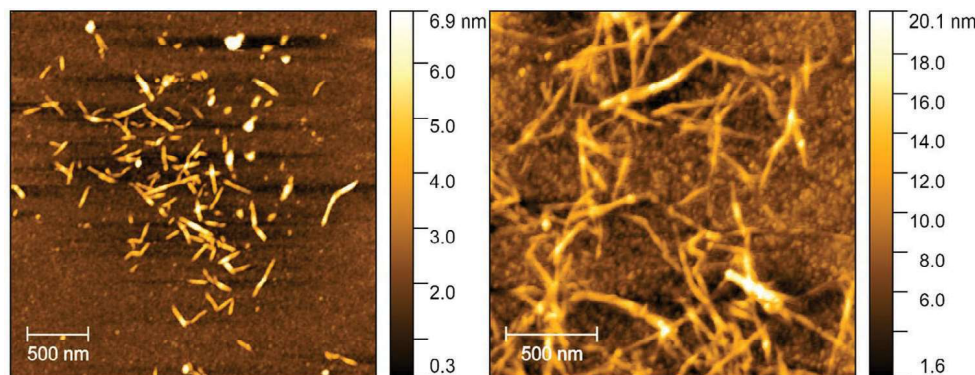


Figure 1. AFM images of CNCs (left panel) and CNFs (right panel).

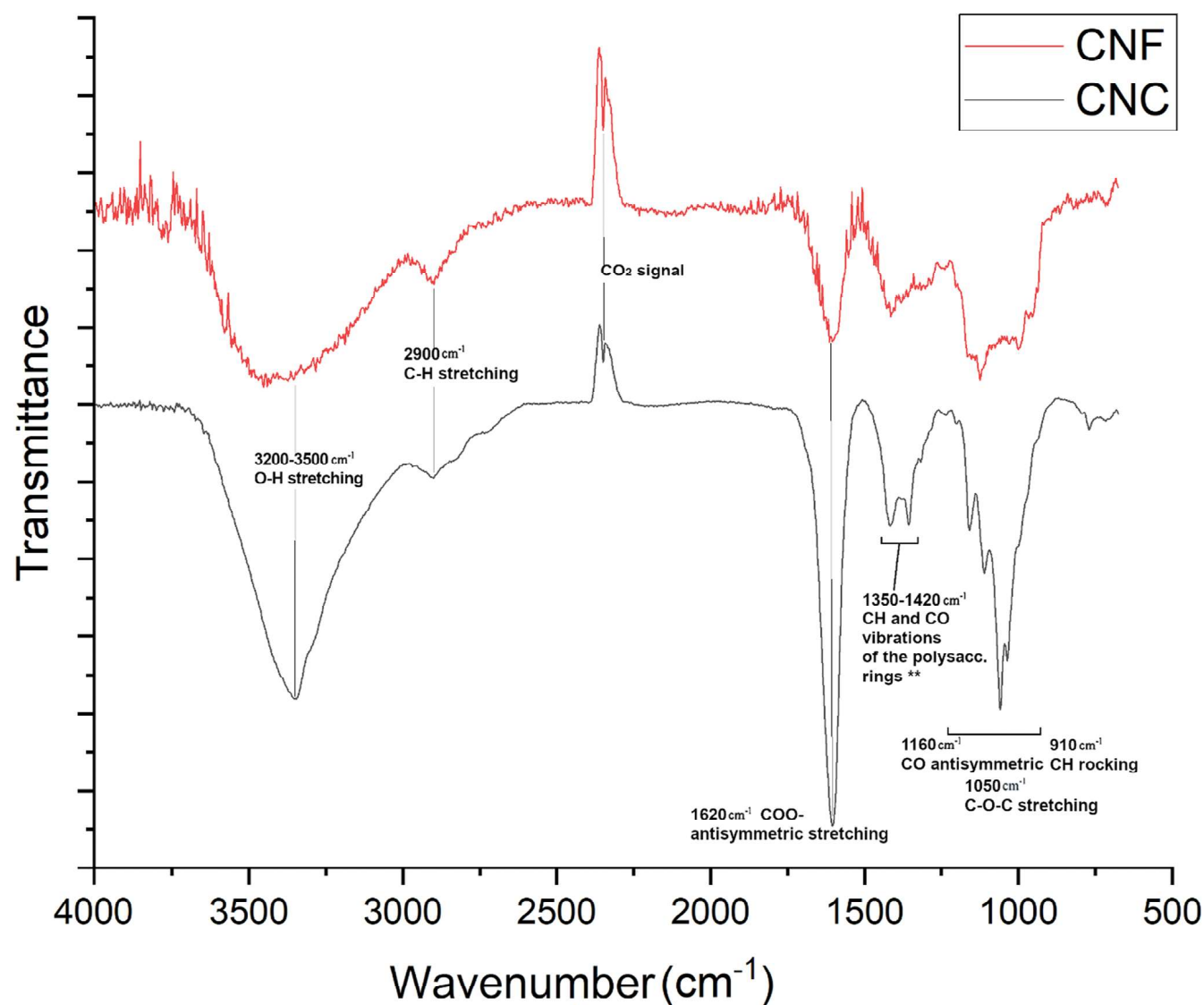


Figure 2. FT-IR spectra of CNCs (black trace) and CNFs (red trace). The spectra were normalized to the intensity of the peak at  $2900\text{ cm}^{-1}$ , taken as internal reference.



**Figure 3.** Suspensions of CNCs (on the left) and CNFs (on the right).

and a broad band corresponding to the stretching vibrations of the O—H bonds of primary and secondary hydroxyl groups within the range 3200–3500  $\text{cm}^{-1}$ .<sup>[43]</sup>

A prominent peak at 1620  $\text{cm}^{-1}$  indicates the presence of carboxylates introduced by the TEMPO-mediated oxidation. The varying degrees of oxidation of CNCs and CNFs become apparent when comparing the intensities of the carboxylate peaks in the spectra of Figure 2, normalized to the peak at 2900  $\text{cm}^{-1}$ , which remains unaffected by the TEMPO-mediated reaction. The normalized spectra reveal a more substantial oxidation of CNCs compared to CNFs, aligning with the milder oxidation conditions used to produce larger sizes and preserve some amorphous regions within CNFs.

The FT-IR findings were confirmed by conductometric titrations, yielding degree of oxidation values of  $0.6 \pm 0.2 \mu\text{mol mg}^{-1}$  and  $1.4 \pm 0.1 \mu\text{mol mg}^{-1}$  for CNFs and CNCs, respectively.

The aqueous suspensions of CNCs and CNFs, as depicted in Figure 3, were evaluated for their physical properties, including the average hydrated size, polydispersity, electrophoretic mobility, and average cross section obtained from AFM images. The summarized results are reported in Table 1.

DLS data revealed an average hydrodynamic size of 652 nm (polydispersity 24.4) and 163 nm (polydispersity 23.3) for CNFs and CNCs, respectively. Notably, high  $\zeta$ -potential values, specifically  $-47.0 \pm 2 \text{ mV}$  and  $-37 \pm 2 \text{ mV}$  at pH 6.0 for CNCs and

**Table 1.** Morphological characteristics of CNCs and CNFs before and after HPH processing.

Sample	Hydrated size <sup>a)</sup> [nm]	Polidispersity <sup>a)</sup>	$\zeta$ -potential <sup>a,b)</sup> [mV]	Cross section <sup>c)</sup> [nm]
CNCs	170	23.3	$-46 \pm 3$	$3.0 \pm 0.5$
CNFs	652	24.4	$-35 \pm 2$	$4.9 \pm 0.5$
CNCs after HPH	155	26.1	$-47 \pm 2$	$4.1 \pm 0.5$
CNFs after HPH	325	37.7	$-30 \pm 2$	$5.0 \pm 0.5$

<sup>a)</sup>The measurements were conducted using a DLS apparatus; <sup>b)</sup>The values were obtained from electrophoretic mobility in aqueous solution; <sup>c)</sup>The cross-section was determined through a statistical analysis of AFM images, utilizing a data set of 900 data samples for the as-prepared CNCs and CNFs and 100 samples for HPH-treated CNCs and CNFs.

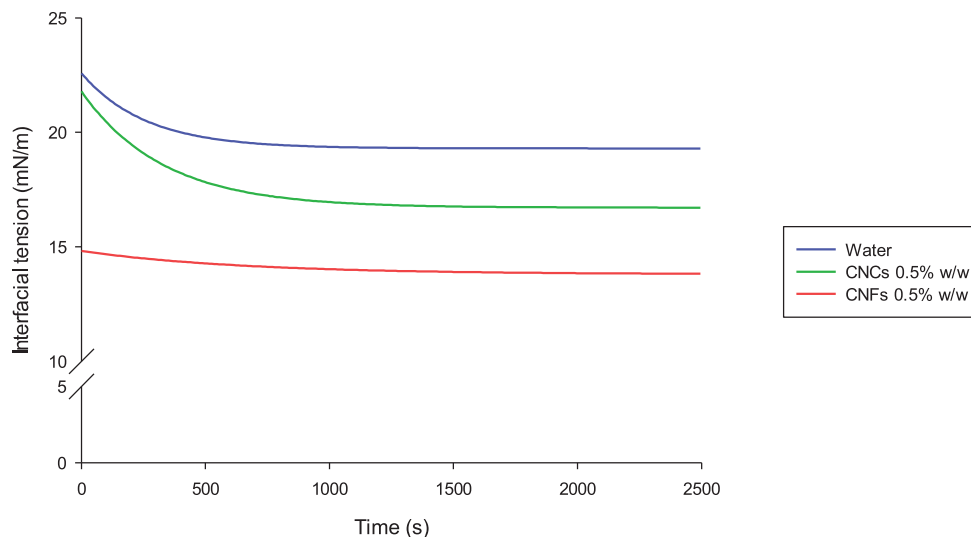
CNFs, respectively (Table 1), underscore the presence of substantial interparticle electrostatic repulsion forces, crucial for colloidal stabilization.<sup>[44]</sup> These findings suggest that CNCs and CNFs share a similar chemical composition, differing primarily in the content of carboxylate groups.

The observed cross-section value for CNCs (3.5 nm) aligns with existing literature data. Conversely, CNFs tend to aggregate into macrofibrils, and the average cross-section typically falls within the range of 18 and 20 nm, decreasing to 7–8 nm when the CNFs surface is highly charged.<sup>[45]</sup> An average value of 5 nm indicates effective defibrillation through ultrasounds.

The distinct length and shape of the NCs used in this study are evident: CNCs exhibit a needle-shaped structure, whereas CNFs appear elongated and partly disordered. Finally, both NCs preparations form stable dispersions, making them promising candidates for Pickering emulsion stabilization.

The wettability of solid particles on oil surfaces is an important factor to stabilize the oil emulsion particles through the adsorption of solid particles on oil surfaces.<sup>[40]</sup> Therefore, the impact of CNCs and CNFs on interfacial phenomena was explored by tracking the change of interfacial tension at the water-oil interface. Figure 4 illustrates the dynamic adsorption behavior of CNCs and CNFs at the water-oil interface, investigated by monitoring the change in interfacial tension ( $\gamma$ ) with adsorption time (0–2500 s) at 25 °C. Upon the addition of both CNCs and CNFs to deionized water, a significant reduction in the interfacial tension of the oil-water interface was observed. Notably, CNFs exhibited a higher reduction than CNCs, suggesting a more pronounced dynamic adsorption behavior and the strong binding of particles to the interface. Once adsorbed, a greater number of CNFs nanoparticles may be able to orient themselves in the interface, given the increased flexibility of the molecules, and prevent droplet coalescence compared to typical molecular surfactants in the emulsion stabilization.<sup>[40]</sup> The interfacial tension of water rapidly decreased within the initial 500 s, due to the adsorption of more hydrophilic oil components, eventually reaching a gradual equilibrium. Over time, both CNCs and CNFs demonstrated a decrease in interfacial tension, converging toward equilibrium values ( $\gamma_\infty$ ). These equilibrium values, estimated using an exponential decay model (Equation 2), were determined to be 16.7 and 13.8  $\text{mN m}^{-1}$  for CNCs and CNFs, respectively.

The  $\gamma_\infty$  value for CNCs was slightly lower than that estimated for pure water (19.2  $\text{mN m}^{-1}$ ), indicating a reduced ability of



**Figure 4.** Peanut oil-water interfacial tension for pure water (—), aqueous suspensions at 0.5 wt% CNCs (—), and 0.5 wt% CNFs (—).

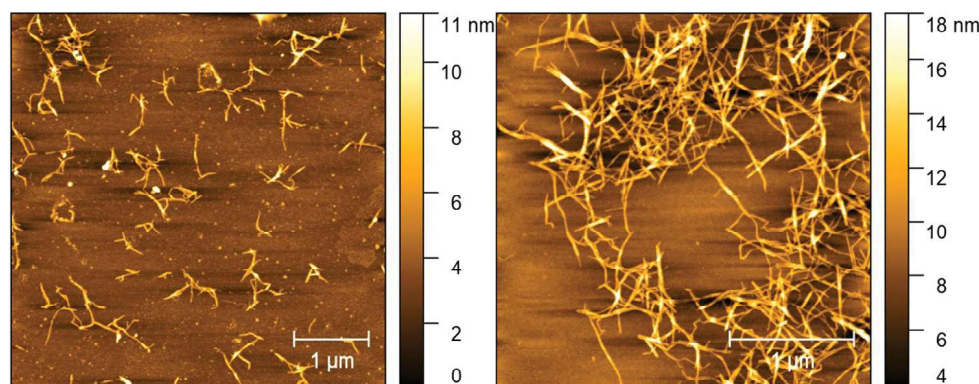
CNCs particles to interact with the oil-water interface. In contrast, CNFs nanoparticles with the lowest interfacial tension corresponded to the maximum number of adsorbed at the water-oil interface, effectively reducing its free energy. This suggests, based on interfacial tension measurements, that CNFs have the potential to be more effective in emulsifying oil and water by adsorbing on the surfaces of oil droplets with high desorption energies, making the O/W Pickering emulsions thermodynamically more stable.<sup>[46]</sup> Moreover, the dense structure network of CNFs and their entangled nature plays a significant role in emulsions' physical properties, leading to act more as a rheological modifier in the continuous water phase than as a Pickering stabilizer.<sup>[47]</sup> It is crucial to consider the effectiveness of emulsifiers in terms of rapidly reducing interfacial tension, strong binding to the interface, and protection against droplet flocculation or coalescence. The interfacial tension values of ionic surfactants, i.e., Tween 20 and Tween 80, and of  $\beta$ -cyclodextrin, commonly used as emulsifiers or stabilizers, have been estimated to be  $\approx 35\text{--}40\text{ mN m}^{-1}$ <sup>[48]</sup> and  $20\text{ mN m}^{-1}$ <sup>[49]</sup> respectively. The higher interfacial tension values for ionic surfactants and  $\beta$ -cyclodextrin oligosaccharide suggest lower adsorption at the oil-water interface compared to

NCs particles, providing insights into the potential of CNCs and CNFs as stabilizers.

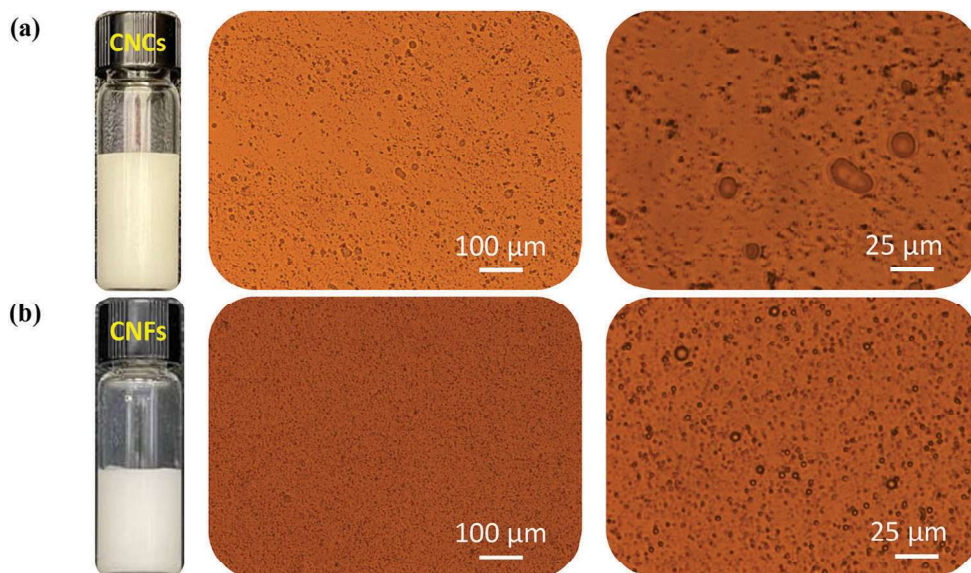
The protocol for stabilizing Pickering emulsion (elaborated details provided later) involves HPH processing at 80 MPa, following the methodology outlined by Pirozzi et al.<sup>[42]</sup> It is worth noting that this treatment could not only impact droplet size but also potentially influence the physical properties of individual NCs' particles. The disruptive energy from HPH induces a dynamic assembly-disaggregation process of the droplets.

Previous studies indicate that HPH processing can effectively reduce the particle length of NCs without altering their functional groups.<sup>[36]</sup> Considering this, the physical characterization of both nanoparticles, CNCs and CNFs, has been conducted after subjecting their aqueous suspensions to HPH processing. The AFM images of HPH-treated NCs are presented in **Figure 5**, and physical parameters are detailed in **Table 1**. These investigations provide insights into the changes induced by HPH on the NCs and enable an assessment of its potential impact on emulsion stabilization.

The results outlined in **Table 1**, along with the comparison between **Figures 1** and **5**, suggest that HPH treatment has a



**Figure 5.** AFM images of CNCs (left panel) and CNFs (right panel) after HPH processing at 80 MPa.



**Figure 6.** Visual observation and micrographs of Pickering emulsion stabilized with a) CNCs and b) CNFs at two different magnifications (10 $\times$  on the left-hand side and 40 $\times$  on the right-hand side).

negligible impact on the size of rod-like CNCs and their electrical interface properties. Conversely, the length of CNFs consistently decreases following HPH treatment. The average hydrated size of CNFs is nearly halved, while the cross-section remains unaffected. The characteristic bending propensity inherent to fibrous nanostructures is still evident in the right panel of Figure 5. Post-HPH treatment, the aspect ratio for CNFs is estimated to be greater than 100, while for CNCs, it is approximately 54. These findings highlight the differential effects of HPH shear and impact forces (elongation, hydrodynamic cavitation, turbulence, and pressure gradient)<sup>[50]</sup> on the two types of NCs and emphasize potential implications for their utilization in Pickering emulsions stabilization. Specifically, CNCs can effectively interact at the oil-water interface and form a robust particle network, thereby enhancing emulsion stability and preventing coalescence and Ostwald ripening, as HPH treatment does not significantly alter their shape and properties. Conversely, HPH causes significant physical changes in CNFs particles, such as breakage of inner bonds (fibrillation) and shortening of the fibers,<sup>[51]</sup> while preserving their properties. The improved fibrillation and the reduction of fiber length makes the fiber more flexible, reducing the bending stiffness of the fiber wall. Shorter CNFs with improved dispersion are a desired effect to improve the efficient formation of a dense and stable particle network at the emulsion interface. Therefore, based on the revealed results, the CNFs particles subjected to HPH treatment during the formation of Pickering emulsions hold great significance for the stabilization effect, preventing droplet aggregation and improving long-term emulsion stability. Remarkably, the size and morphology of NCs are a critical factor indicating emulsifying activity and stability, as well as their applications. Based on the results discussed above, the following two points are proposed for NCs-stabilized Pickering emulsions' mechanisms: i) CNCs stabilize O/W emulsions by forming a dense layer at the oil droplet surface, as well as between adjacent oil droplets, due to their nanosize and highly negative  $\zeta$ -potential already before the HPH treatment, and ii) CNFs stabilize O/W

emulsions by forming a layer of entangled fibrils network at oil droplet surfaces, due to size halved and the defibrillation degree after the HPH treatment.

## 2.2. Characterization of NCs-Stabilized Pickering Emulsions

The formation, morphology, and time behavior of Pickering emulsions stabilized with CNCs and CNFs were examined through optical imaging, while the emulsions size distributions were measured using laser diffraction.

Figure 6 shows the microstructure of freshly prepared Pickering emulsions stabilized with CNCs (Figure 6a) and CNFs (Figure 6b) at a 5 wt% oil phase. In both cases, oil droplets of relatively uniform size were observed, with CNFs-stabilized Pickering emulsion exhibiting a better-textured overall structure. The oil droplets in CNFs-stabilized emulsions displayed a spherical structure with a uniform size of  $\approx 3 \mu\text{m}$ . CNCs-stabilized emulsions are still uniform in size; however, it is likely that a fraction of CNCs particles remain partially dispersed in water, as suggested by Bertsh and Fisher.<sup>[52]</sup> These authors demonstrated that CNCs at the fluid interphase tend to be almost fully submerged in the water phase due to their low desorption energy from the interphase, and hence show a dynamic adsorption/desorption behavior. Conversely, nanofibrillated CNFs, coupled with the thickening effect of the residual short amorphous tract, facilitated more efficient entrapment of oil droplets, resulting in the development of a 3D emulsified structure. It can be speculated that the enhanced entanglement capacity facilitated the bridging of neighboring droplets, creating an interconnected droplet-CNFs fiber 3D network. Overall, the micrographs in Figure 6 are in agreement with previous observations in the preparation of Pickering emulsions stabilized by CNFs.<sup>[42]</sup>

Remarkably, despite the reported differences in interfacial tension and  $\zeta$ -potential, both CNCs and CNFs displayed outstanding stability against droplet coalescence, with no observed phase sep-

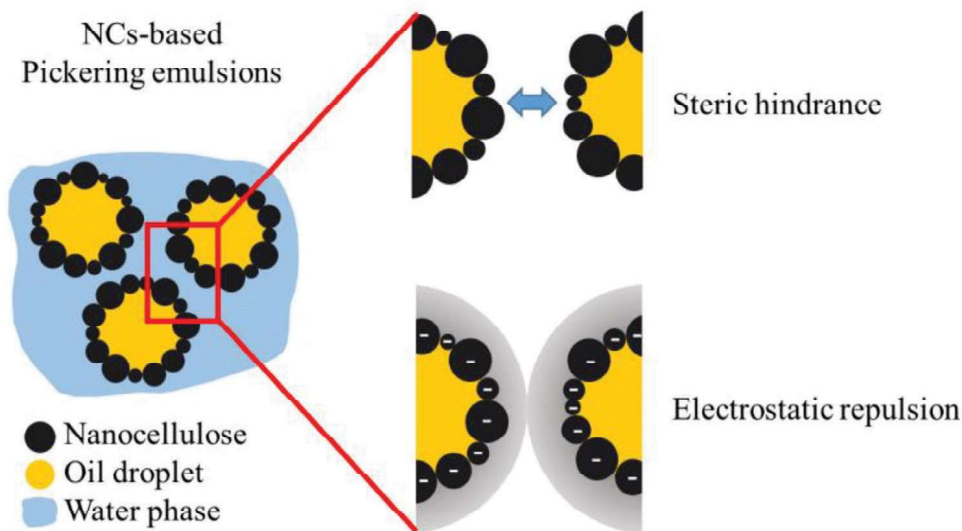


Figure 7. Electrostatic stabilization interactions of CNCs- and CNFs-based Pickering emulsions.

aration during refrigerated storage at 4 °C. This remarkable stability is likely attributed to the effective strong repulsive forces (steric hindrance and electrostatic repulsion stabilization mechanisms) provided by both CNCs and CNFs that inhibit droplet aggregation, ensuring the long-term integrity and functionality of the Pickering emulsions (Figure 7).

The impact of the emulsion processing in this study was investigated in terms of droplet size distribution (Figure 8) and mean droplet diameters (Table 2) for both the coarse emulsions (after high-shear mixing (HSM)) and the final emulsions (after HPH treatment). The measured size distributions align with the micrographs in Figure 6, indicating a significant effect of the process intensity on size distribution.

Notably, the droplet characteristic diameters and the distribution span exhibited a sharp decrease after the application of HPH treatment. The particle size distribution of emulsions treated by HSM was multimodal, with three peaks (CNCs) and two peaks (CNFs) in the distribution curve within a range from 1 to 100  $\mu\text{m}$ . In contrast, after HPH treatment, the volume fraction of small droplets increased, resulting in monomodal and narrow droplet size distribution with span values of 1.2 and 1.4, and  $d(0.9)$  values of 2.23 and 2.92  $\mu\text{m}$  for CNCs and CNFs, respectively. Similarly,  $d(0.1)$  value was reduced to sub-micrometric size range, and  $d(0.5)$  to the micrometric size range for both HPH emulsions. The volume mean diameters  $D[4,3]$  were in the range of 1.4–1.8  $\mu\text{m}$ , and the surface mean diameters  $D[3,2]$  in the range of 1.2–1.4  $\mu\text{m}$  (Table 2). Low  $D[3,2]$  values are generally associated with higher kinetic stability due to the reduction of the effects of gravitational phase separation, as the droplet separation velocity is proportional to their square radius.<sup>[53]</sup> Moreover, the droplet size, influenced by the application of HPH mechanical treatment, is known to have an important impact on the rheology of emulsions<sup>[42]</sup> and, as a consequence, to play a crucial role in controlling the physical properties of emulsions for food, cosmetics, and various industrial applications. Fine emulsions with decreased droplet size and span values have much higher vis-

cosities and storage moduli than the corresponding coarse emulsions, as found by Pal.<sup>[54]</sup> This phenomenon could be ascribed to different reasons: i) the mean distance of separation between the droplets decreases with the decrease in droplet size, leading to an increase in hydrodynamic interaction and viscosity; ii) the effective dispersed-phase concentration increases; and iii) the width of the particle size distribution decreases.

NCs are expected to stabilize the Pickering emulsions through two primary mechanisms, as schematic represented in Figure 9: i) stabilization via the formation of interfacial film/envelopes of particles surrounding oil droplets of the dispersed phase, that prevents them from coalescing; and ii) encapsulation of the oil droplets in a 3D network<sup>[26]</sup> of aggregated nanoparticles, that inhibits their movement.

The extent of surface coverage plays a pivotal role in Pickering stabilization, governed by the interfacial properties of the NCs. To explore this aspect, the relationship between emulsion size and the volume fraction of the dispersed phase (i.e., oil) was investigated and the emulsion coverage, defined as the maximum number of NCs entrapped at the droplet interface, was estimated. Interestingly, the percentage coverage of emulsions stabilized with different types of NCs, after HPH processing, exceeded 100% (377% and 131% for CNCs and CNFs, respectively). This result confirms that NCs create an efficient interfacial coating, with a denser arrangement observed for CNCs. This finding is in line with the observations of Kalashnikova et al.<sup>[55]</sup> who suggested that the higher steric hindrance of longer CNCs limits denser packing at the interface, leading to porous multilayered profiles. The strong interaction observed between the cellulose nanostructure and the oil droplets, as indicated by the present data, plays a crucial role in enhancing the physical stability of the Pickering emulsions. This interaction can contribute to various stabilization mechanisms, including i) increasing the viscosity of the continuous phase, ii) reducing the emulsion droplets size, and/or iii) minimizing the difference in density between the continuous phase and the dispersed one.<sup>[55–59]</sup> To further under-