

Renewable Resources Derived Cellulose Nanocrystal Stimuli Responsive Pickering Emulsions

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As an environmentally friendly and sustainable nanoparticle stabilizer of Pickering emulsions, cellulose nanocrystal (CNC) has attracted attention because of its sustainable and biodegradable characteristics. Despite its distinct amphiphilic character as an ideal nanomaterial to replace traditionally non-sustainable surfactant emulsifiers, its long-term stability and lack of responses from external stimuli [e.g., pH, temperature, and carbon dioxide (CO₂)] are the critical issues to be addressed. The solutions for all of these questions in terms of CNCs and its responsive Pickering emulsions are systemically discussed in this review.

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INTRODUCTION

Pickering emulsions were discovered independently by Walter Ramsden (Ramsden 1903) and Spencer Umfreville Pickering (Pickering 1907). The phenomenon uses solid particles sized at nanometers or micrometers instead of molecular surfactants as emulsifiers, and these adsorb at the water and oil interface. Compared to surfactants, these kinds of emulsions have unique traits, such as high stability and low dosage utilization of stabilizing materials. It has broad applications in the biomedical, agricultural engineering, and food science fields. Contrary to surfactants, the inorganic particles or polymers that stabilize Pickering emulsions are more stable for a longer time (Jia *et al.* 2016; Ngwabebhoh *et al.* 2018). However, most inorganic particles and polymer emulsifiers are nondegradable. Therefore, alternative materials are needed for these solid particles. Renewable resources such as nanocellulose (CNC), cellulose nanofibrils, and chitin have advantages of biodegradability and sustainability, which are ideal attributes of particle emulsifiers of Pickering emulsions, as shown in Fig. 1 (Calabrese *et al.* 2018; Franco *et al.* 2020). CNCs efficiently stabilize oil/water interfaces resulting from their amphiphilic surface nature. This amphiphilic character is attributed to its hydrophilic edge of cellulose chains and hydrophobic face. Thus, CNCs are likely to form oil/water emulsions typically prepared through mechanical blends of CNC aqueous dispersion and oil. As a result, CNCs stabilize the emulsions by absorbing at the oil/water interfaces. The droplet stabilization mechanism by using CNC is directly related to the steric repulsion and electrostatic interactions among droplets, and thus CNC is an effective barrier to cover the oil droplets.

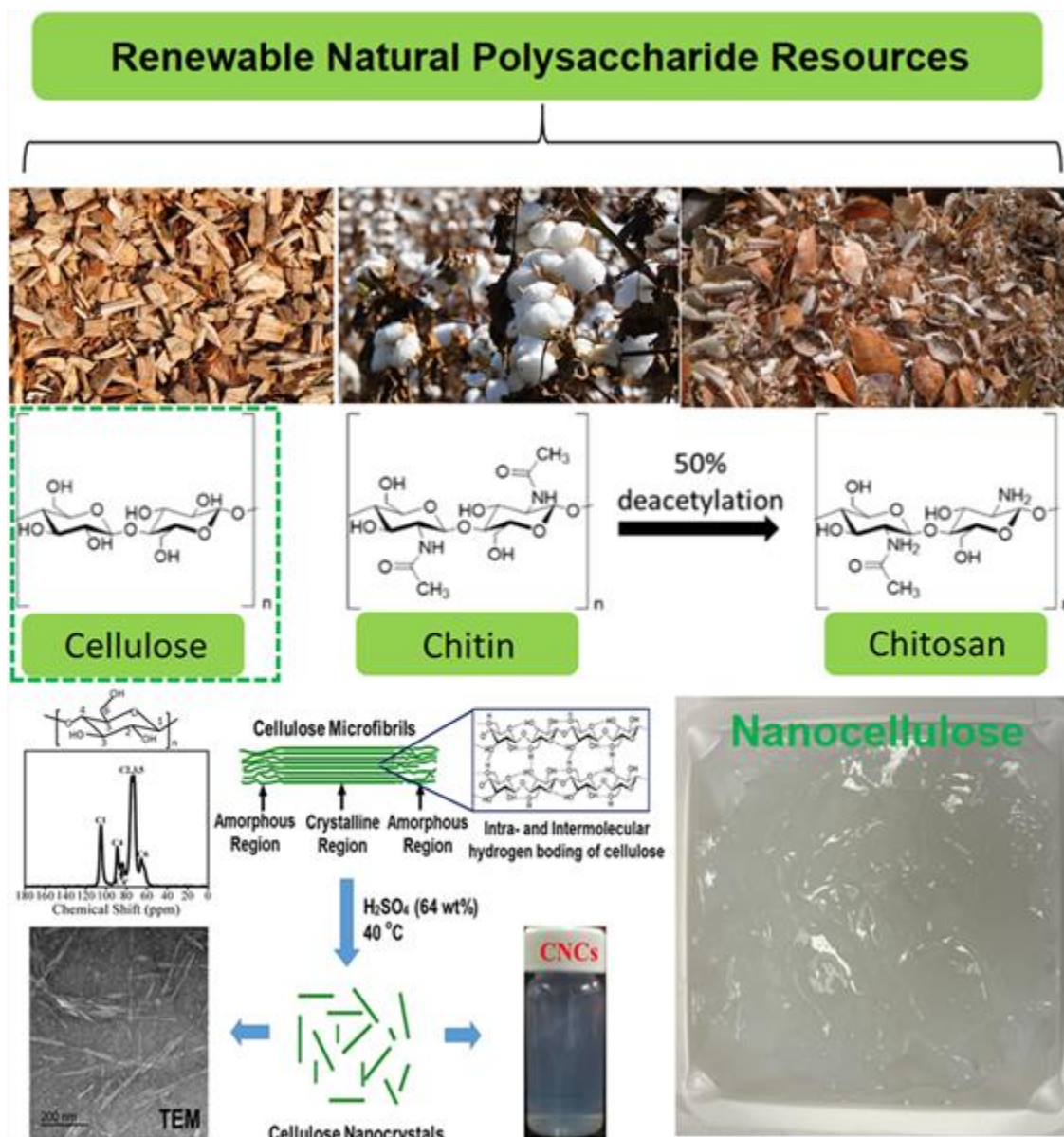


Fig. 1. Renewable resources derived nanocellulose, chitosan, and chitin biomaterials (Calabrese *et al.* 2018). Reprinted with permission from Elsevier Publishing Co.

However, unmodified CNC is not an effective emulsifier because of its highly hydrophilic and abundant -OH groups. Despite the amphiphilic character of CNCs for Pickering emulsion stabilizers, the long-term stability and lack of responses from external stimuli [*e.g.*, pH, temperature, and carbon dioxide (CO_2)] as the stabilizers of Pickering emulsions are the critical issues to be addressed. Thus, the basic factors governing CNC Pickering emulsion stabilization and design of CNC responsive emulsions are investigated systemically in this review. As this review is about the emulsion stabilization, and its stabilization is sensitive to creaming, sedimentation, and flocculation. Important concepts in terms of these behaviors are defined here. Creaming or sedimentation means that the rise or fall of droplets to the surface or bottom of an emulsion, respectively, which are reversible as droplet interfaces do not fuse. Flocculation refers to the droplets dispersed in an

emulsion aggregate resulted from attractions of stabilizing particles. However, their interfaces don't merge, so it is also reversible. For coalescence, a big droplet is formed due to the merging of droplets, and it leads to phase separation eventually, which is irreversible.

BASIC FACTORS GOVERNING NANOCELLULOSE STABILIZED PICKERING EMULSIONS

Nanocellulose with Varied Aspect Ratios, Shapes, Surface Charges and Dosages

The CNC particle size is an important factor in regulating oil droplet size and emulsion stabilization. Compared with relatively large particles, small particles forms smaller oil droplets. As the particle concentration is constant, the larger particle has a less surface than the smaller particle. Thus, a relatively higher interface coverage is achieved for the smaller particle. Therefore, the smaller particle stabilizes a higher volume of emulsions at a fixed particle concentration. However, the stability is determined by repulsion between particles residing on different droplets. The repulsive force is proportional to particle size. As the larger particle results in more repulsion between droplets, large repulsion leads to emulsions with more stable performance and less chance of creaming and sedimentation. CNCs from bacterial cellulose with different sizes were used as the Pickering emulsion stabilizer, and the results also indicated the oil droplet stabilized with CNCs in smaller size was not vulnerable to coalescence (Li *et al.* 2019) and the correlation of cellulose particle size and emulsification stability was also established (Niu *et al.* 2017).

The CNC particle shape determines the emulsion property, and CNC shape is usually evaluated by aspect ratio defining by the ratio of CNC particle length and its diameter. Most emulsions are stabilized with spherical particles. Compared with spherical particles, needle-like CNC particles have relatively high coverage at the oil-water interface, and the resulting emulsion has dense interfacial packing and better stability as needle-like CNCs experiences shape induced attractive capillary forces when deposited at fluid-fluid interactions, and such interactions also drive particles toward each other, while spherical particles have no such interactions (Dugyala *et al.* 2013). These capillary forces depend on the aspect ratio of particles. Namely, the strength of such interactions increases with large aspect ratio. For instance, for emulsions stabilized by needle-like particles, the aggregated viscoelastic networks were established around the curved oil-water interface of emulsion droplets due to these capillary force attractions, thereby preventing them from coalescence and phase separation.

The surface charge of CNCs is important in regulating emulsion stabilization. The charges on CNC surface govern the electrostatic repulsion among droplets and protect it from coalescence. As the most common method, the preparation of CNCs from a sulfuric acid hydrolysis method replaces some of surface hydroxyl groups with sulfate ester groups. Its suspension dispersion and electrostatic repulsion with each other benefit from surface charges, leading to oil/water emulsion stability. Thus, the emulsion stability is closely dependent on the CNC surface charges. Therefore, the electrostatic repulsion decreases as surface charge reduces, which causes the particle aggregation and destabilization of emulsions. Sulfated CNC particles with varied sulfur contents have been investigated as particle stabilizers of triglyceride oil/water emulsions (Zhang *et al.* 2019a). If surface charge is too high, CNC particle does not adsorb at the oil/water interface. Using pH and

oppositely charged molecules to tailor the surface charge on the emulsion particle is the primary method. For instance, CNC particle surface charge is tailored by grafting polymers with the oppositely charged molecules to stabilize the emulsion. De-sulfonation treatment and electrostatic repulsion by opposite charge ions have been explored for tailoring highly charged CNCs to regulating emulsion stabilization (Pandey *et al.* 2018).

The emulsion properties are also influenced by CNC dosage and its ratio to oils. In general, increase in the CNC dosages contributes to the increase in the viscosity of emulsions and reduction in the emulsion droplet size as high dosage of CNCs promotes its network structure formation or offer more steric hindrance to cease aggregation, thereby enhancing emulsion stability. The emulsion stability is directly related to the ratio of CNCs to oils. As the ratio of CNCs to oils is much low, Pickering emulsions are unstable with large oil release and phase separation due to its insufficient coverage in the droplet interface (Meirelles *et al.* 2020). Followed by the increased ratio of CNCs to oils, it becomes sufficient to cover the initial surface of droplets, and droplets are stabilized by strong electrostatic repulsion between droplets. However, as the ratio of CNCs to oils further increases, the oil droplet surface is saturated with CNCs, so its excess is dispersed in the continuous phase, thereby increasing viscosity of dispersion phase and alter droplet formation and coalescence (Bai *et al.* 2019). In addition to the stabilizing particles, shear stress applied during emulsification as another factor governs emulsion property. The shear stress during the ultrasonication, micro-fluidization, and high-pressure homogenization treatment enables to refine coarse emulsions by droplet breakup, thereby favoring the formation of smaller droplets. For the high-pressure homogenizer and microfluidizer, the emulsion droplets are propelled over a valve via high pressure and then broken into small ones. For the ultrasonication, coalescence phenomenon is usually observed in the emulsions produced (Costa *et al.* 2018).

Nanocellulose from Different Sources and Extraction Methods

Large amounts of agroindustrial residues are produced each year, and most of these materials are usually not treated appropriately, which causes serious resource waste. However, these agricultural wastes are ideal precursors for extraction of CNCs, such as ginkgo seed shell (Costa *et al.* 2018), banana peels (Seo *et al.* 2021), *Piper kadsura* stem (Tiong *et al.* 2020), argan shell (Kasiri *et al.* 2018), asparagus (Wu *et al.* 2020), cotton (Yan *et al.* 2017), and rice bran (Angkuratipakorn *et al.* 2017). The source of CNCs affects their emulsion properties, as shown in Table 1.

Table 1. Renewable Source Derived Nanocellulose to Tailoring Emulsion Stability

Renewable Sources	Emulsion Performance	Functionality
Ginkgo seed shells (Costa <i>et al.</i> 2018)	Low (storage of 1-6 days)	Stability
Kelp (Wu <i>et al.</i> 2020)	High (storage of 30 days)	Stability
Banana peels (Seo <i>et al.</i> 2021)	High (storage of 10 days)	Stability
<i>Piper kadsura</i> stem (Tiong <i>et al.</i> 2020)	High (storage of 90 days)	Oil Recovery
Argan shell (Kasiri <i>et al.</i> 2018)	High (storage of 28 days)	Stability
Pistachio shell (Winuprasith <i>et al.</i> 2013)	High (storage of 80 days)	Stability
<i>Miscanthus floridulus</i> straw (Li <i>et al.</i> 2019)	High (storage of 14 days)	Food Science
Rice bran (Angkuratipakorn <i>et al.</i> 2017)	High (storage of 28 days)	Oxidative Stability
Cotton (Yan <i>et al.</i> 2017)	Unknown (no data)	Stability
Bacterial cellulose (Li <i>et al.</i> 2019)	Unknown (no data)	Stability
Mangosteen rind (Winuprasith <i>et al.</i> 2015)	High (storage of 80 days)	Stability
Asparagus (Wu <i>et al.</i> 2020)	Low (storage of few hours)	Stability

For instance, ginkgo seed shell contains plenty of cellulose, which is an ideal source for extraction of CNCs (Costa *et al.* 2018). The CNCs derived from the ginkgo seed shell with different lengths are extracted *via* high pressure homogenization, and the resulting CNCs can be applied for Pickering emulsion stabilizer. Short CNCs have a better performance for reducing emulsion interface tensions.

Chemical methods can be used for isolation of CNCs. For instance, the CNCs and microfibrillated cellulose (CNFs) were also prepared from pistachio shell and ground mangosteen rind through acid hydrolysis (Winuprasith and Suphantharika 2013) and chemical treatment, respectively. The resulting CNCs as nanoparticle stabilizers made it possible to maintain the Pickering emulsion performance (Li *et al.* 2019). Agricultural byproducts are also potential sources for preparation of CNCs. Argan shell residues have been used for preparation of CNFs through chemical treatment and high-pressure homogenizer (Kasiri *et al.* 2018). The mangosteen rind residue containing 60 to 70% cellulose contents is produced in large quantities each year, so it is a new potential lignocellulosic precursor for extraction of CNCs. Mangosteen rind derived CNFs stabilized emulsions are stable for more than 2 months (Winuprasith and Suphantharika 2015). Waste wood chips and bacterial cellulose are also ideal sources for CNC extraction. For instance, bacterial cellulose derived CNCs prepared *via* combined sulfuric acid hydrolysis and hydrogen peroxide oxidation was studied as emulsion stabilizers (Li *et al.* 2013).

Considering different chemical methods for CNC preparation, it is also possible to influence the emulsion performance as different methods enable to produce CNCs varied in surface functional group content, particle size, and morphology, which is directly related to emulsion stabilization. 2,2,6,6-tetramethylpiperidin-1-yloxy (TEMPO) oxidation, acid hydrolysis and ammonium persulfate (APS) oxidation are the primary methods for the preparation of CNCs. The sulfuric acid hydrolysis for preparation of CNCs is shown in Fig. 1. For instance, bifunctional CNCs made *via* acid hydrolysis are able to stabilize emulsions (Li *et al.* 2018). CNC surface with negative charges prepared from the TEMPO and APS oxidation method promotes its dispersion in aqueous solution and contributes to the electrostatic repulsion, thereby resulting in the enhanced emulsion stability (Mikulcová *et al.* 2018; Leung *et al.* 2011). For instance, carboxylated CNCs extracted from ammonium persulfate oxidation method have been used for the particle stabilizer of oregano essential oil Pickering emulsion, and the antimicrobial performance of its Pickering emulsions has been investigated. Carboxylated CNC stabilized emulsions inhibit bacterial growth (Mikulcová *et al.* 2018). However, the CNC extraction method has no large influence on its ability to stabilize Pickering emulsions (Wen *et al.* 2014).

NANOCELLULOSE MODIFICATION GOVERNING STABILIZED PICKERING EMULSIONS

Modified Nanocellulose Tailoring Pickering Emulsion Stability

Despite the amphiphilic character of CNCs as Pickering emulsion stabilizers, long-term stability is still an important issue as the strong hydrophilic CNCs produce large, unstable oil droplets, which easily coalesce. To tailor the hydrophilicity of CNC particle, the feasible way is to graft hydrophobic groups on its surface. The chemical and physical surface modification methods are shown in Table 2. Although pristine CNCs stabilized emulsions have been investigated, surface modification is still the common strategy to tailor the particle partitioning among oil and water phases of emulsions and improve its

stability performance (Hiranphinyophat *et al.* 2019; Kedzior *et al.* 2021). Various physical modification methods *via* tailoring hydrogen bonding and electrostatic interactions have been developed for tailoring surface property of CNCs to enhance emulsion long-term stability. The CNC surface was also modified by the polymer adsorption *via* electrostatic interactions (Ahsan *et al.* 2019). The improved colloidal stability of cationic CNCs stabilized emulsions depends on the electrostatic complexation at the oil-water interface, and its stabilization resulted from two effects: network formation and electrostatic complexation at liquid-liquid interface (Ahsan *et al.* 2019; Silva *et al.* 2020).

Table 2. Cellulose Modification Strategies for Tailoring Pickering Emulsion Property

Modification	Surface Modifiers	Functionality
Physical	Phosphoric acid (Jia <i>et al.</i> 2013)	Stability
Physical	Sodium carboxymethyl cellulose (Ahsan <i>et al.</i> 2019)	Stability
Chemical	Trimethylammonium (Silva <i>et al.</i> 2020)	Antimicrobial property
Chemical	Periodate chlorite oxidation and reductive amination (Ojala <i>et al.</i> 2016)	Stability
Chemical	Phenyltrimethylammonium chloride (Gong <i>et al.</i> 2017)	Cosmetic products
Chemical	Vinyl acetate (Sèbe <i>et al.</i> 2013)	Stability
Chemical	Vinyl cinnamate (Sèbe <i>et al.</i> 2013)	Stability
Chemical	Bromoisobutyl bromide (Dupont <i>et al.</i> 2020)	Porous material
Chemical	Phenyltrimethoxysilane (Zhang <i>et al.</i> 2019b)	Stability
Chemical	Dodecylamine (Liu <i>et al.</i> 2019)	Stability
Chemical	Acetic anhydride (Xu <i>et al.</i> 2018)	Stability
Chemical	Octenyl succinic anhydride (Chen <i>et al.</i> 2018)	High internal phase emulsion
Chemical	Carboxymethyl cellulose sodium (Yu <i>et al.</i> 2021)	Antimicrobial property

Vinyl acetate, vinyl cinnamate, acetic anhydride, trimethylammonium, bromoisobutyl bromide, and phenyltrimethoxysilane functional groups have been used to tailor the hydrophilicity of the CNC surface to improve emulsion performance (Sèbe *et al.* 2013; Liu *et al.* 2019; Yu *et al.* 2015; Tang *et al.* 2019; Dupont *et al.* 2020; Silva *et al.* 2020; Zhang *et al.* 2020). For instance, the surface of wood cellulose was oxidized followed by surface modification with phenyltrimethylammonium chloride to graft the hydrophobic phenyl groups, resulting in enhanced emulsion properties (Gong *et al.* 2017). Octenyl succinic anhydride tailored CNCs have been used as Pickering emulsion stabilizers as well (Chen *et al.* 2017), and its degree of substitute on the influence of stabilization of Pickering emulsion was investigated. The enhanced emulsion stabilization results from the network formation among modified CNC particle and oil droplets and particle adsorption at the liquid-liquid interface, thereby reducing the oil droplet aggregation and coalescence (Xie *et al.* 2020). It is also crucial to understand the assembly and adsorption of CNCs in the liquid-liquid interface of emulsions. Acetylated cellulose nanofibrils (CNFs) have been used as the particle stabilizer of emulsions, and the energy barrier driven by the electrostatic repulsions primarily determine the CNF particle adsorption at liquid-liquid interface (Xu *et al.* 2020). Different from the directly conventional surface modification, the released functional groups by the destruction of CNC backbone has also been used for the grafting modification to tailor CNC hydrophilicity. For instance, grafting dodecylamine to 2,3-dialdehyde cellulose particles was studied for governing Pickering emulsion performance as shown in Fig. 2 (Visanko *et al.* 2014). Bifunctional CNCs containing carboxylic and

butylamino groups were prepared *via* periodate-chlorite oxidation and reductive amination reaction, and the modified CNC particle stabilized Pickering emulsions showed the improved oil droplet stabilization, with no oil droplet coalescence (Ojala *et al.* 2016). In addition to the improved stabilization, the surface modification of CNCs impart emulsions with unique properties. Carboxymethyl cellulose sodium modified CNCs used as stabilizers of clove essential oil resulted in Pickering emulsions with high antimicrobial activity (Yu *et al.* 2021). In addition to its surface modification, CNC reducing end modification is a novel approach. The unique aspect of the reducing end modification is enabling to maintain the surface sulfate ester groups of CNCs and its cellulose background backbone prepared from sulfuric acid hydrolysis, so the amphiphilic character can be well preserved even after modification with polymer chains at its reducing end. Polystyrene (PS) grafted on the CNC end through reductive amination endows CNCs with amphiphilic features, and the PS grafted CNCs with different number average molecular weight of PS segments maintain the emulsion stabilization for several months without phase separation as shown in Fig. 2 (Tang *et al.* 2018).

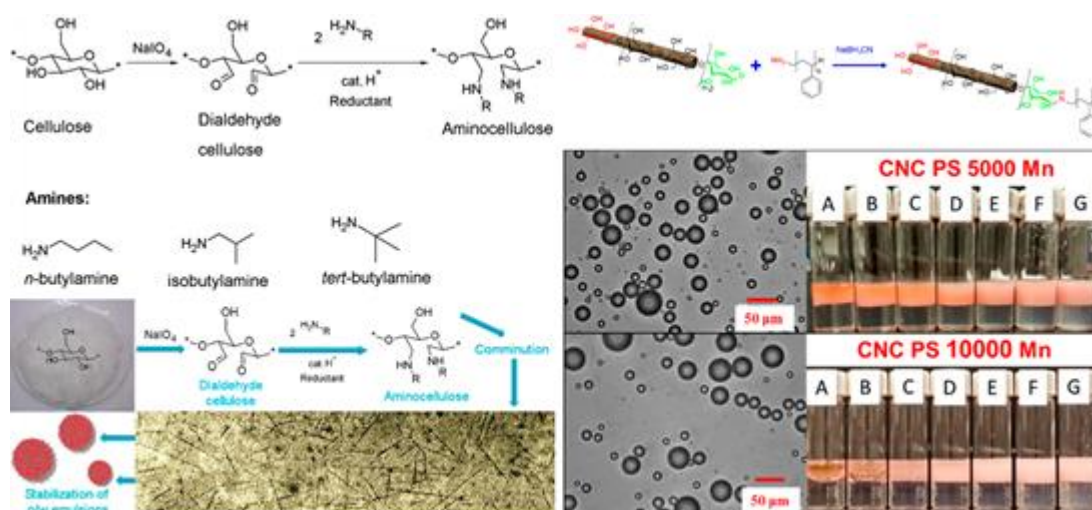


Fig. 2. Nanocellulose surface and reducing end modification for tailoring its Pickering emulsion stability (Visanko *et al.* 2014; Tang *et al.* 2018). Reprinted with permission from Visanko *et al.* (2014), *Biomacromolecules*, 15, 2769-2775. Copyright 2014, American Chemical Society and Tang *et al.* (2018), *Langmuir*, 34, 12897-12905. Copyright 2018, American Chemical Society.

Synergistic Combination of Nanocellulose and Other Biomaterials

Wood derived lignin, chitosan, chitin, alginate, or protein are used as synergistic components to tailor the CNC surface and its Pickering emulsion stabilization property. The primary approach to form the complex as the particle stabilizer is by the surface charge interactions. As chitin and chitosan with unique surface groups commonly works as synergistic particle stabilizer, the CNC and chitin mixture was used as the particle stabilizer of emulsions, and results demonstrated 3D network was formed from nanofibers in water phase and fixed oil droplets from moving around and thus enhanced the creaming stability (Lv *et al.* 2021). The mixture of anionic nanocellulose and cationic nanochitin was also employed for stabilizing lipid Pickering emulsion. The complexation particles stabilized emulsions have a better performance than single CNC nanofibers in term of stabilization of oil droplets to coalescence (Zhou *et al.* 2020). The hydroxypropyl methylcellulose, carboxymethyl cellulose sodium, bacterial cellulose also combined with CNCs as

synergistic particle stabilizers of camellia oil Pickering emulsions, and the emulsions had improved performance (Xie *et al.* 2019; Franc *et al.* 2020; Martins *et al.* 2020; Zhang *et al.* 2020; Tanaka *et al.* 2023). The addition of CNC and synergistic protein influences the emulsion performance (Pindřáková *et al.* 2019; Zhang *et al.* 2019c). The nanocomplex particle morphology also has influence on the emulsion performance. Chitosan is an ideal biomaterial for preparation of Pickering emulsion applied in the food science field. However, chitosan has a low solubility in neutral water (Takeshita *et al.* 2017), so its surface modification with glycidyltrimethylammonium chloride (GTMAC) with positive charges enables to be enhanced in its water solubility. The nanocomplex from charge interactions among negative CNCs and positive GTMAC modified chitosan can also well stabilize food Pickering emulsions. CNCs prepared sulfuric acid hydrolysis possesses negative charges on its surface and enables to form the nanocomplex with GTMAC modified chitosan. However, sulfuric acid as the strong acid hydrolyzed CNCs is not suitable for food science field application. Thus, phosphoric acid (H_3PO_4) as a weak acid is an ideal alternative of the sulfuric acid for CNC preparation with negative charges by esterification reactions to stabilize Pickering emulsion (Patoary *et al.* 2023; Espinosa *et al.* 2013). For example, the hard sphere and random coil morphology of nanocomplexes of glycidyltrimethylammonium chloride modified chitosan (GTMAC-M-C) and phosphorylated CNCs (PCNCs) were prepared by varying ratios of GTMAC-M-C and PCNCs, and Pickering emulsions emulsified with this complex particle were stable over 3 months and had no phase separation. The complex particle stabilized oil droplets also had no coalescence (Baek *et al.* 2019)

The synergistic biomaterial as particle stabilizer also imparts the emulsions with new property. For instance, the lignocellulose nanofibrils mixed with residual lignin showed the improved hydrophobicity and had a better performance as the Pickering emulsion stabilizer. The resulting emulsions also showed the antioxidant and UV absorption property, which was attributed to the residual lignin (Guo *et al.* 2013). CNCs and lauric alginate complexes were also used as Pickering emulsions stabilizer and the resulting nanoparticles-stabilized-emulsion had good physical and oxidative stability (Angkuratipakorn *et al.* 2020).

STIMULI RESPONSIVE NANOCELLULOSE PICKERING EMULSIONS

As the nature of thermodynamic stability of CNCs stabilized Pickering emulsions, it is hard to achieve its demulsification even in long-term storage. Therefore, it is desirable to design switchable surface CNC particles that make it possible to tailor the stable and unstable status. Thus, the temporarily stabilizing and subsequently demulsifying of emulsions enables them to satisfy applications on special occasions, *e.g.*, transporting oil products or releasing a drug. Therefore, the development of switchable emulsions under the external stimuli (*e.g.*, pH, CO_2 and temperature) have attracted increasing attention.

Temperature Responsive Pickering Emulsions

Temperature-responsive CNC Pickering emulsions have been explored. The surface functionalized temperature responsive polymer chains *via* covalent and non-covalent modification are used to design thermally responsive CNC Pickering emulsions. The temperature responsive polymers are ethylene oxide (EO) and propylene oxide (PO) copolymer, poly(2-isopropoxy-2-oxo-1,3,2-dioxaphospholane) (PIPP), poly(N-isopropyl-

acrylamide) (PNIPAM), poly(oligo-ethylenoxide) methacrylate, and poly(2-(dimethyl-amino) ethyl methacrylate) (PDMAEMA). For instance, PIPP grafted CNCs *via* the ring open polymerization have been prepared, and the resulted modified CNCs has low critical solution temperature at 45 °C (Hiranphinyophat *et al.* 2019). The modified CNC particles enabled to regular the emulsification and demulsification transition *via* external temperature variations, thereby achieving the smart responsive property of the emulsions.

PNIPAM, as a well-known thermal responsive polymer, has unique properties, such as biocompatibility and phase transition temperature similar to body temperature. So it has been studied in the areas of biomedical and smart responsive delivery systems. Thus, PNIPAM grafted CNC *via* controlled radical polymerization has been prepared, and the resulting modified CNCs enabled to stabilize the emulsions for more than few months (Hemraz *et al.* 2014). As the temperature increased to its phase transition point at 32 °C as low critical solution temperature, the demulsification was clearly seen. PDMAEMA is another thermoresponsive polymer that has been extensively studied. The PDMAEMA grafted CNCs *via* the controlled radical polymerization was prepared, and its low critical solution temperature phase transition point was determined to be 50 °C. As the temperature increased above 50 °C, rapid demulsification was observed (Tang *et al.* 2014). Besides, ethylene oxide and propylene oxide copolymer are thermal responsive polymers with a phase transition temperature at approximately 16 to 30 °C. Ethylene oxide and propylene oxide copolymer grafted CNCs was prepared *via* controlled electrostatic interactions (Ren *et al.* 2019), and the resulted copolymer modified CNC exhibited temperature responsive demulsification property as shown in Fig. 3.

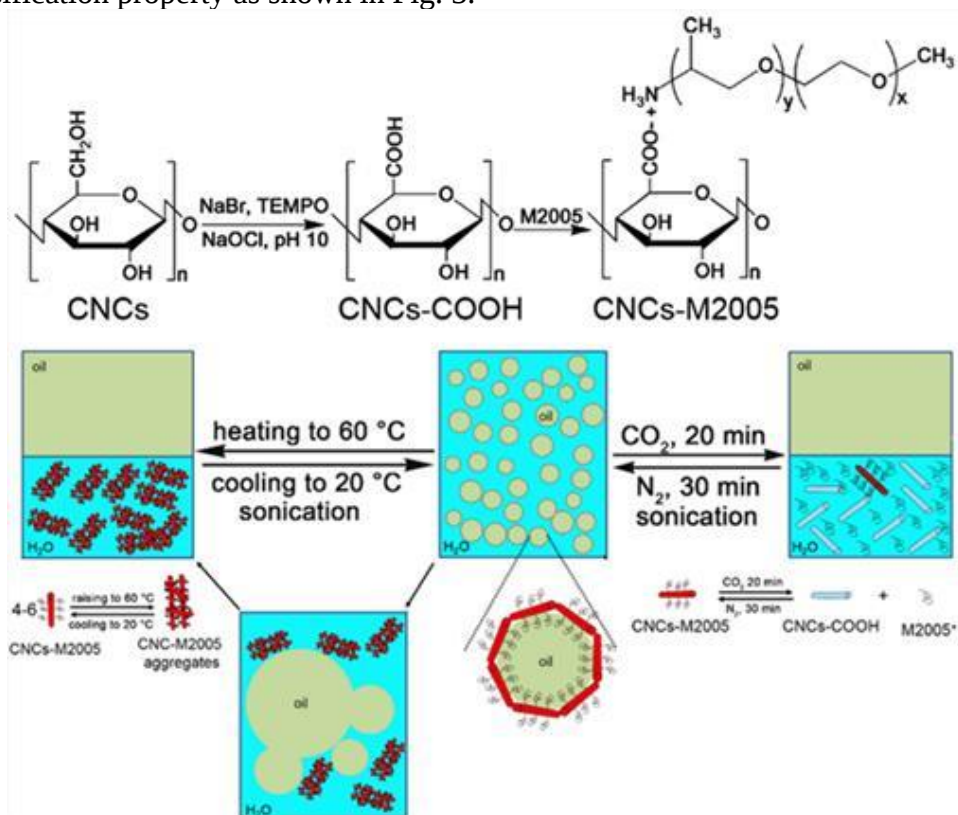


Fig. 3. Schematic illustration of copolymer ethylene oxide (EO) and propylene oxide (PO) grafted CNC dual-responsive Pickering emulsions (Ren *et al.* 2019). Reprinted with permission from Ren *et al.* (2019), *Langmuir* 35, 13663-13670. Copyright 2019, American Chemical Society.

CO₂-responsive Pickering Emulsions

The design of CO₂-responsive Pickering emulsions has attracted significant attention in the last few years, as CO₂ is easily available and low cost. The basic principle of CO₂ responsive Pickering emulsion is briefly explained here. As CO₂ gas passes into emulsions and then transforms into dissolved gas normally as carbonic acid in the equilibrium state. The acidity variation in the emulsion system enables to alter the ionic change of moieties or chain segments on the surface of CNC particles, thereby triggering CNC surface wettability variation. By adding nitrogen gas into the emulsion, the CO₂ in the system enables to be easily removed, thereby achieving CO₂ switchable property.

The design of CO₂ responsive CNC nanoparticles can be achieved *via* covalent and non-covalent approaches. The ethylene oxide and propylene oxide copolymer have both temperature- and CO₂-responsive features, so it is commonly used for design of CO₂ responsive emulsion. For instance, this copolymer grafted CNCs was prepared *via* the controlled electrostatic interactions, and the resulted modified CNC allowed it to stabilize Pickering emulsions and exhibited the CO₂ responsive demulsification property after bubbling CO₂ into the emulsion system resulted from the dissociation of grafted copolymer chains on surface of CNCs, as shown in Fig. 3 (Ren *et al.* 2019). Poly[N-3-(dimethyl amino) propyl methacrylamide] (PDMA PMAm) and PDEAEMA are also CO₂ responsive polymers that have been studied for CO₂ responsive Pickering emulsions. For instance, PDMA PMAm and PDEAEMA grafted CNC with different grafting density and molecular weight has been prepared *via* the nitroxide-mediate polymerization, and the resulted modified CNCs Pickering emulsions enabled it to achieve reversible transition from demulsification to emulsification by external CO₂ stimulation (Glasing *et al.* 2018). Moreover, poly(o-nitrobenzyl acrylate) and PDMAEMA grafted CNCs were prepared *via* the controlled radical polymerization, and the resulted modified CNCs showed the temperature, CO₂ and light responsive property. The CNC grafted copolymers as the stabilizer of Pickering emulsions showed the reversible CO₂ responsive property in term of emulsification and demulsification upon external N₂/CO₂ stimuli (Tajmoradi *et al.* 2021).

pH-responsive Pickering Emulsions

pH is also an important environmental factor to be considered for the design of smart responsive emulsions. However, only a few studies have been reported in terms of pH responsive CNC Pickering emulsion up to now. The direct way to impart non-responsive CNCs with pH responsive property is through covalent or non-covalent CNC surface modification with pH-responsive polymers. Polyethyleneimine (PEI) is a pH-sensitive cationic polymer, which is widely investigated for the design of smart functional materials and responsive emulsions. For instance, the amphiphilic nanoparticles, the CNC surface grafted with hydrophilic polyethyleneimine, were prepared through reductive amine reaction (Li *et al.* 2021). Then they were used as solid particles stabilizer of organo essential oil/water Pickering emulsions. As the primary, secondary and tertiary amine groups of PEI are sensitive to pH value, the pH-responsive PEI grafted CNCs made it possible to tailor the surface wettability property of amphiphilic CNC nanoparticles under the external pH stimulation and regular the demulsification performance of emulsions, thereby controlling antimicrobial functional agent release (Meng *et al.* 2023). Due to its pH responsive property, PDMAEMA is widely studied in the areas of biomedical, drug delivery, and functional emulsions. For instance, PDMAEMA-grafted CNCs synthesized *via* the conventional free radical polymerization were used for the temperature-responsive Pickering emulsion. By regulation of pH values, the Pickering emulsion could achieve the

reversible transition in term of demulsification and emulsion (Tang *et al.* 2014). The benzyl-polyethyleneimine modified CNCs prepared *via* the reductive amine reaction was also used for the design of pH-responsive Pickering emulsion. By adjusting pH value, the amphiphilic benzyl-polyethyleneimine grafted CNCs made it possible to regulate the emulsion transition from stable to unstable condition (Xiao *et al.* 2020). The pH-responsive CNC Pickering emulsions have potential for application in controlled releases of biomedical agents. The research in terms of targeted delivery of hydrophobic bioactive molecules has given attention. However, its low water solubility limits its drug delivery application. Using oil-in-water Pickering emulsion as carriers is potential for its delivery to target sites as hydrophobic bioactive molecules dispersed in the oil phase can be encapsulated in pH modifier tailored CNC Pickering emulsions (Chen *et al.* 2020; Shirjandi *et al.* 2022).

CONCLUSIONS AND FUTURE PROSPECTS

Cellulose nanocrystals (CNCs) are ideal biomaterials with which to replace surfactant emulsifiers that have a negative influence on the environment. CNCs as particle stabilizers of Pickering emulsions have biodegradability and sustainability features. The basic factors of CNCs (*e.g.*, extraction sources, aspect ratios, surface charge) governing Pickering emulsion stabilization performance have been systemically summarized in this review. Other biomaterials as synergistic particle stabilizers working together with CNCs to tailor the emulsion stabilizations are also available. Different physical and chemical CNC modification methods can be used to tailor emulsion long-term stability. The design of stimuli-responsive CNC Pickering emulsion (*e.g.*, temperature, pH, and CO₂) *via* covalent and non-covalent modification strategies are interesting areas for further research.

However, there are major challenges for CNC stabilized Pickering emulsions. The traditional CNC surface modification strategies destroy the surface functional groups or damage cellulose backbone structure; new modification methods are required (Zhang *et al.* 2023). Reduced ending modification of CNCs preserves the CNC structure and surface groups, which is a promising strategy for further study. For instance, the modification on CNC reducing ends may make it possible to prepare the amphiphilic molecules *via* reductive amination reaction that had excellent performance on the Pickering emulsion stabilization. The development of novel extraction methods to prepare CNCs is also in high demand, *e.g.*, with usage of deep eutectic solvents (Ling *et al.* 2019). The electrostatic interaction as non-covalent modification or dynamic covalent bond is a promising way for further tailor emulsion property compared to the CNC surface modification, as the strong hydrogen bonding interactions in CNCs results in its difficulty in dispersion in aqueous solution (Ren *et al.* 2018). Moreover, the smart responsive CNC Pickering emulsions primarily focuses on single temperature responsive property, while other types of stimuli responsive emulsions like pH and CO₂ responsive are still less reported up to now. Considering the limited responsive polymers reported in design of responsive emulsions, more responsive polymers need to be explored in the future, such as poly(N-vinylcaprolactam), a temperature-responsive polymer. Finally, the design of smart responsive CNC Pickering emulsions relies on the controlled radical polymerization such as atom transfer radical polymerization and reversible addition-fragmentation chain-transfer polymerization. However, its complex reaction and purification procedures in controlled radical polymerization for design of CNC functional materials should influence

its performance as particle stabilizers. Therefore, developing novel polymerization methods is a priority (Mendoza *et al.* 2023).

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