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Cellulose nanocrystals as water-in-oil Pickering emulsifiers via intercalative modification

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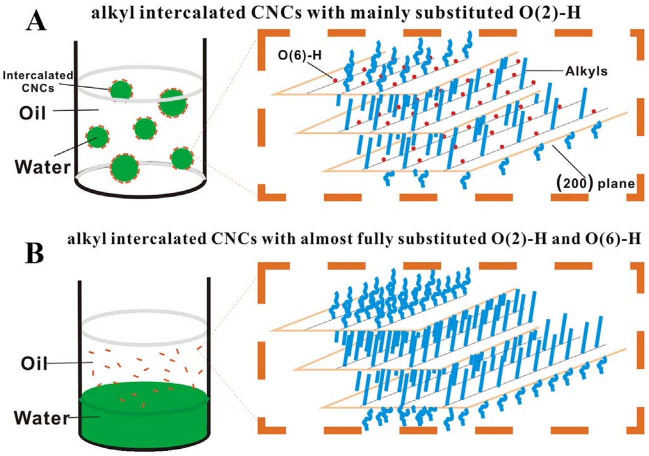
GRAPHICAL ABSTRACT



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ABSTRACT

A novel water-in-soybean oil Pickering emulsifier based on CNCs was fabricated via the intercalative chemical reaction between *n*-octadecyl isocyanates and hydroxyl groups in CNCs. The structural variations of alkyl intercalated CNCs with different degrees of substitution for hydroxyl groups were studied by TEM, AFM, FTIR, XRD, elemental analysis and liquid DSC. It is shown that O(2)H/O(6)H instead of O(3)H in CNCs were substituted after intercalative modification. And the particle thickness was increased after the intercalation, due to the enlargement of the basal spacing of (200) lattice plane in CNCs. While their cross section dimensions were unvaried. The structural variations in alkyl intercalated CNCs on their emulsifying capacity were further studied. Particle length has the insignificant influence on the emulsifying capacity. Alkyl intercalated CNCs with different particle lengths failed to stabilize water-in-soybean oil Pickering emulsion droplets, if O(2)H/O(6)H hydroxyl groups were fully substituted with alkyls. Alkyl intercalated CNCs with appropriate amounts of substituted hydroxyl groups possessed a good emulsifying capacity. After the initial coalescence, the average droplet size and its distribution polydispersity remained nearly constant with one year of storage. Results shown that alkyl intercalated CNCs with different degrees of substitution for hydroxyl groups had the similar interfacial tension at

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the soybean oil-water interface, the similar molecular arrangement of internal intercalated alkyls but different contact angles. These indicated that emulsifying capacity was mainly related to their surface alkyl chains. Besides, water-in-soybean oil Pickering emulsions stabilized by alkyl intercalated CNCs were from steric hindrance rather than interfacial tension reduction mechanism.

1. Introduction

Emulsion, a mixture of two or more liquids that are normally immiscible, has provided broad applications in various fields such as food, cosmetic, petroleum, pharmaceutical industries and material fabrications [1,2]. The addition of surface-active species is essential to achieve stable emulsions [3]. Small molecular weight surfactants, amphiphilic polymers, and proteins have been widely used as emulsifiers, while stabilized emulsions are thermodynamically unstable and tend to breakdown over time due to physicochemical mechanisms such as gravitational separation, flocculation, coalescence, Ostwald ripening, and phase inversion [4]. In the early 20th century, solid colloidal particles with appropriate wettability were reported to irreversibly adsorb at the immiscible liquids interface and had higher emulsifying capacities [5,6]. Particles-stabilized emulsions, commonly referred as Pickering emulsions, therefore have attracted considerable attentions in past decades, because of the high stability against coalescence and Ostwald ripening, the reduction or removal of surfactants from emulsion recipes, as well as due to advances in nanotechnology that allow us to create and characterize nanoscale structures in new ways [7–10].

A wide variety of solid particles has been used as Pickering emulsifiers, including latex, silica, clay, alumina, titanium oxides, iron oxide, organic particles, and polymer Janus particles [8,3,11–13]. In comparison with spherical particles, particles with the high aspect ratio are particularly efficient in the stabilization of emulsions and foams [14], because anisotropic shape fundamentally alters geometric aspects such as the percolation threshold, packing issues and capillary interactions specific to interfaces [15].

Cellulose nanocrystals (CNCs) are rod-shaped nanoparticles [16]. Their particle dimensions and reactive functional groups are dependent upon raw cellulose materials and hydrolysis conditions [17–19]. CNCs are a promising candidate in stabilizing Pickering emulsions, because of their adjustable dimension, abundant hydroxyl groups for the wettability adjustment, as well as the good toxicity profile and environmental benefits [20]. Till now, CNCs have been widely reported to stabilize oil-in-water Pickering emulsions either through the surface modification [21–31], or through the addition of electrolytes for preventing electrostatic repulsion [32–36], or through the appropriate choice of cellulose raw materials [37,38] or through controlling hydrolysis conditions [39,40]. On the contrary, water-in-oil Pickering emulsions stabilized by CNCs are few.

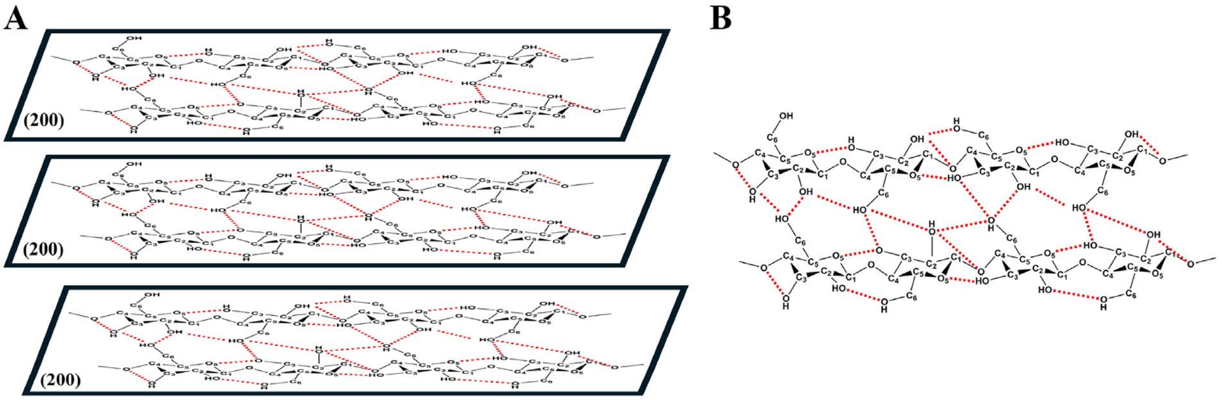
CNCs have the highly orientated crystallite structure due to cellulose microfibril biosynthesis [41]. In CNCs I_β (monoclinic structure) polymorph for instance, parallel stacking of cellulose chains in the (200) plane is present (Scheme 1A). And strong intrachain hydrogen bonding O(3)-H···O(5) bond and intra- and inter-chain bonding O(2) H···O(6) and O(6)H···O(2) bonds are prevalent (Scheme 1B) [42]. Weaker intersheet interactions such as CH···O hydrogen boning and van der Waals forces are responsible for the neighboring (200) planes [41]. Therefore, CNCs have the potential as a layered host candidate for fabricating intercalated nanocomposites [43]. The intercalative modification could be used to adjust the wettability of CNCs for the stabilization of water-in-oil emulsion, as observed for numerous layered emulsifiers exemplified by layered double hydroxides, layered niobates, and clays [44–46].

Herein, hydrophobic *n*-octadecyl isocyanates were intercalated in CNCs through the intercalative chemical reaction between their terminal groups and O(2)-H/O(6)-H hydroxyl groups on CNCs (200) lattice planes. Alkyl intercalated CNCs with different degrees of substitution for O(2)-H/O(6)-H hydroxyl groups were prepared and used to formulate water-in-oil emulsions. The structure of alkyl intercalated CNCs was investigated by FTIR spectroscopy, elemental analysis, X-ray Diffraction (XRD) and liquid Differential Scanning Calorimetry (DSC). The structural variation of alkyl intercalated CNCs was further related to the change of emulsifying capacity. The present study would provide a scientific basis for the fabrication of emulsifiers based on CNCs via the intercalative modification and also further extent the application of intercalated CNCs.

2. Material and methods

2.1. Materials

Cellulose filters (softwood sulfite pulp) were purchased from the Xinhua Paper Mill (Hangzhou, China). N-octadecyl isocyanate and dibutyl dilauryl were purchased from Sigma-Aldrich (France). Sulfuric acid, ethanol, dichloromethane and toluene were purchased from the Beijing Chemical Reagent Company (Beijing, China) and were used without further purification. Reagent grade soybean oil was purchased from Aladdin Company (Shanghai, China). Toluene was dried and purified according to standard procedures. Dialysis bags (Mw cut off 14,000) were purchased from the Greenbird Company (Shanghai, China).



Scheme 1. Schematic drawings of A) parallel stacking of cellulose chains in the (200) plane of CNCs I_β polymorph, B) the dominant hydrogen-bond network in cellulose I_β chains at the origin of the unit cell according to a previous study [42].