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Modulating the zeta potential of cellulose nanocrystals using salts and surfactants

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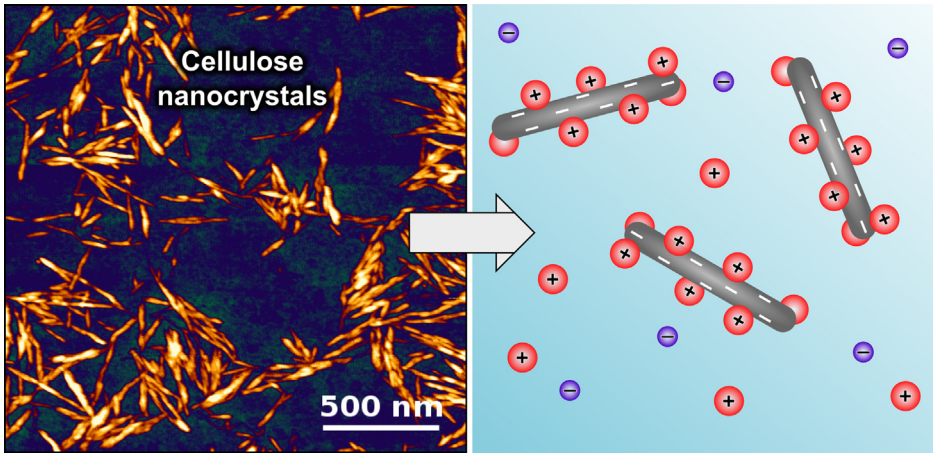
HIGHLIGHTS

- Zeta potential of cellulose nanocrystals is explored as a function of additives.
- Hofmeister-type specific ion effects modulate ion adsorption.
- Surfactant adsorption can increase or reverse surface charge.
- Film roughness from cellulose nanocrystals depends on suspension zeta potential.

GRAPHICAL ABSTRACT



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ABSTRACT

The zeta potential of cellulose nanocrystal (CNC) aqueous dispersions was studied as a function of solution conditions, including changing pH and different electrolyte identities and concentrations. A range of electrolytes that spans typical Hofmeister/hydrophobic effects was explored, along with both cationic and anionic surfactants. A subtle interplay of electrostatic and hydrophobic effects in ion adsorption was uncovered, including evidence of charge reversal and supercharging when hydrophobic surfactants are added to aqueous CNC dispersions. The apparent effects of zeta potential on dispersion stability were explored by using atomic force microscopy (AFM) to determine the roughness of resulting CNC films. The root mean square roughness (RMS) of these cellulose films was unaffected by the presence of surfactants (achieving a constant value of ~9 nm), but scaled inversely and non-linearly with the zeta potential of the CNC suspension while using the ionic salts from ~2 nm to 10 nm, indicating a facile method for the control of cellulose film roughness.

Abbreviations: NCC, nanocellulose crystals; AFM, atomic force microscopy; RMS, root mean square; MCC, microcrystalline cellulose; cmc, critical micelle concentration.

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1. Introduction

Cellulosic nanomaterials – including cellulose nanocrystals (CNC), cellulose nanofibres (CNF) [1,2] along with their composites are promising materials for many novel applications [3–5] owing to their unique properties that include excellent mechanical strength [6], self-assembly, liquid crystalline behavior [7,8] and optical properties ranging from transparent to translucent [9]. Controlled acid hydrolysis of native cellulose sources using sulfuric acid is commonly used to synthesise rod-shaped cellulose nanocrystals [10], which are electrostatically stabilized [11] by the sulfate ester moieties [12] on their surfaces. The acid hydrolysis typically results in the formation of cellulose nanocrystals of width 5–10 nm and length 100–300 nm [13].

In aqueous handling of colloidal dispersions, the electrical-double layer [14] is a key feature controlling stability; the extent of the electrical double-layer – modulated by particle surface charge and screening effects – is much affected by the concentration of counter-ions and the nature of the electrolytes used. This important component in the colloidal stability of aqueous suspensions can be determined by zeta potential measurements [15,16]. However, the addition of salts and electrolytes may also affect the amount and distribution of charge on particle surfaces, and even the hydrophobic/hydrophilic ratio, depending on the nature of the salt added [17].

Several studies have reported the effect of added salt concentration on the colloidal stability of CNC. For example, Zhong et al. [18] studied the effect of simple electrolytes like NaCl and $CaCl_2$ on the colloidal stability of CNC. They showed that the zeta potential of CNC became less negative upon addition of Na^+ and Ca^{2+} counter-ions, attributed to an electrostatic screening effect. They also studied the effect of anionic surfactants like sodium dodecyl sulfate (SDS) and polymers such as sodium carboxymethyl cellulose (NaCMC) on the zeta potential of CNC, and found that the zeta potential became more negative. Yu et al. [19] highlighted that polymer concentration, ionic strength and pH influence the colloidal stability when studying polystyrene sulfate latex particles with comparable surface chemistry. Dhar, Au, Berry & Tam [20] studied the interaction between CNC and tetradecyltrimethylammonium bromide (TTAB) – a cationic surfactant. Upon increasing the TTAB concentration, a charge reversal from negative to positive was observed. Jackson et al. [21] studied the effect of another cationic surfactant, CTAB (cetyltrimethylammonium bromide) concentration on the zeta potential of CNC. At higher CTAB concentrations, flocculation was observed, indicating a clear interaction between CTAB and CNC. The binding interaction between CNC and CTAB was also confirmed by the increasingly positive zeta potential of CNC upon increasing the CTAB concentration. A cationic substituent EPTMAC (2,3-epoxypropyl-trimethylammonium chloride) was used to surface functionalize CNC, yielding cationic hydroxypropyl-trimethylammonium chloride groups on the CNC surface [22]. After treatment with EPTMAC, a charge reversal from −39 mV to +30 mV was observed in the CNC zeta-potential.

From these studies, a complex picture emerges in which salt and surfactant interactions can have varied roles on the dispersion stability of CNC, motivating a systematic study to account for the effects at play. In this work, the primary objective is to systematically quantify and understand the effect that salt identity and concentration has on the zeta potential of CNC dispersions. The salt characteristics of most interest are the valency, charge and hydrophobicity of the ions. The second objective is to determine the importance that CNC zeta potential has on engineering applications – specifically film formation. For this study, we examine the effect of CNC zeta potential on the roughness of cellulose films formed by spin coating CNC suspensions of various inherent zeta potential.

2. Experimental

2.1. Materials

Sodium chloride (NaCl), calcium chloride ($CaCl_2{\cdot}2H_2O$), potassium iodide (KI) and anhydrous sodium acetate (NaOAc) were from Merck (analysis grade) and used as received. Tetramethylammonium bromide (reagent grade) was from Sigma-Aldrich, and cetyltrimethylammonium bromide (CTAB, >99%) and sodium dodecyl sulfate (SDS, >90%) were purchased from ChemSupply, SA and used as received. For pH adjustment, sodium hydroxide (NaOH, 99%) and hydrochloric acid (HCl) were used. For the preparation of cellulose nanocrystals, microcrystalline cellulose (MCC, type 101, Sigma-Aldrich) was used along with sulfuric acid (95–98%). Water used was from a Millipore Direct-Q 5, with a minimum resistivity of 18.4 MΩ cm.

2.2. CNC preparation

Preparation of CNC was performed as per the method described by Bondeson, Mathew & Oksman [23]. Firstly, 2 g of microcrystalline cellulose was dispersed in 22.5 mL deionized (DI) water. The suspension was then placed in an ice bath with stirring for about 10–15 min at 500 rpm. Drop-wise addition of sulfuric acid (21.5 mL) was made to the above suspension, after which it was heated to 45 °C, and maintained at this temperature with stirring for 2 h at 500 rpm. The suspension was diluted with cold water (200 mL) to quench the reaction. Using centrifugation (30 min, 5000 rpm, 20 °C), the solid was isolated and resuspended in 50 mL DI water. Repeated centrifugations followed by ultrasonication (Digitech, 100 W ultrasonic cleaner) in between were carried out so as to isolate the CNC from dissolved impurities. For further purification, dialysis (regenerated Fisher brand cellulose dialysis membrane, with molecular weight cut off 12,000–14,000 Da) of recovered supernatants against distilled water was carried out for 5–6 days at room temperature. The water used for dialysis was changed every 6 h. Ultrasonication of the resultant colloidal dispersion was used to ensure full redispersion, and the CNC were then freeze-dried (FreeZone Plus 4.5) for 4–5 days to obtain the solid CNC. For zeta potential measurements, 1 mg mL^{-1} of freeze-dried CNC was redispered in the required solution via ultrasonication. For AFM measurements, the pre freeze-dried CNC (concentration 0.53 mg mL^{-1}) was used.

2.3. Instrumentation techniques

Zeta potential of CNC dispersions was measured using the phase analysis light scattering (PALS) mode on a dynamic light scattering system (DLS, NanoBrook Omni, Brookhaven Corporation). The pH of the suspensions was examined before and after measurements, and HCl and NaOH were used to adjust the pH to required values. Atomic force microscopy (AFM, JPK Nanowizard 3) was used (in alternating contact, AC mode) to obtain images of CNC morphology, along with particle size and root mean square (RMS) roughness analysis. For obtaining the particle size of the CNC, 200 individual crystals were analysed, and the average length and height (i.e. thickness) was calculated. To explore the chemical functionality and crystallinity of the synthesised CNC, Fourier transform infrared spectroscopy (Cary 630 FTIR, Agilent technologies) and powder X-ray diffraction (Eco D8 Advance, Bruker) were used. For FTIR measurements, the single-reflection diamond attenuated total reflectance (ATR) sampling accessory of the instrument was used. The spectra shown are an average of 20 scans; no further manipulation of the data was made. The powder X-ray spectra were collected using a 1 kW Cu source and SSD160 ultrafast 1-dimensional detector; the source