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Synthesis of amine functionalized cellulose nanocrystals: optimization and characterization

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ABSTRACT

A simple protocol was used to prepare amine functionalized cellulose nanocrystals (CNC–NH_2). In the first step, epichlorohydrin (EPH) was reacted with ammonium hydroxide to produce 2-hydroxy-3-chloro propylamine (HCPA). In the next step, HCPA was grafted to CNC using the etherification reaction in an organic solution media. Various reaction parameters, such as time, temperature, and reactant molar ratio were performed to determine the optimal reaction conditions. The final product (CNC–NH_2(T)) was dialyzed for a week. Further purification via centrifugation yielded the sediment (CNC–NH_2(P)) and supernatant (POLY–NH_2). The presence of amine groups on the surface of modified CNC was confirmed by FTIR and the amine content was determined by potentiometric titration and elemental analysis. A high amine content of 2.2 and 0.6 mmol amine/g was achieved for CNC–NH_2(T) and CNC–NH_2(P), respectively. Zeta potential measurements confirmed the charge reversal of amine CNC from positive to negative when the pH was increased from 3 to 10. The flocculation of amine functionalized CNC due to its interactions with a negatively charged surfactant namely, sodium dodecyl sulfate (SDS) was investigated at pH 4. It showed promising results for applications, such as in flocculation of fine dispersions in water treatment. This simple and versatile synthetic method to produce high amine content CNC can be used for further conjugation as required for various applications.

1. Introduction

Cellulose nanocrystals (CNC)—rigid rod-like nanoparticles obtained by acid hydrolysis of pulp fibers have received increasing interests over the last 10 years. The non-toxicity, biocompatibility, and biodegradability of CNC along with its robust physical properties, such as large surface area, mechanical strength, and the presence of abundant surface hydroxyl groups offer interesting opportunity for their use in different fields.[1] In addition, further surface modification of CNC expands its usefulness in many product formulations. The primary hydroxyl groups could be converted to aldehyde, carboxylic acid and amine functionalities. Cationic modification of cellulose and its derivatives is of interest due to their utility in several key industrial sectors, such as water treatment.[2] In a recent study, the surface of CNC was cationically modified with 4-(1-bromoethyl/bromomethyl) benzoic acid, pyridine in organic media. It was reported that a high degree of substitution leading to a zeta potential of +59.0 mV was observed.[3]

Modification of the surface of CNC with primary amine groups not only introduces cationic charge on the surface of CNC in acid medium, but it can also be used for the conjugation of biomolecules to CNC for biomedical applications.[4] The importance of polysaccharides with amine functional groups in biological systems has led to an increase in research activity in this field.[5,6]

Different forms of cellulose have been modified with amine groups via several synthetic methods. In one study, a three-step procedure was used to prepare 6-deoxy-6-amino cellulose derivatives. First, cellulose was tosylated and reacted with sodium azide, where the azide was reduced to amine using $CoBr_2$/2,2′-bypridine/$NaBH_4$ system.[7] Amine cellulose esters were also prepared by reactions involving lactam ring opening in the presence of N-methyl-2-pyrolidone and *p*-toluenesulphonic acid chloride.[8] In

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another study, polyampholytic amino cellulose sulfates were prepared by the tosylation of C-6 carbon followed by the introduction of sulfate groups using trioxide/pyridine complex. Further nucleophilic displacement of tosyl groups by different amines yielded various types of cellulose with different types of amine functional groups.[9]

In recent years, amine functionalized CNCs have been produced via different synthetic routes. In one study, researchers decorated the surface of CNC with epoxide groups via reaction with epichlorohydrin (EPH) in sodium hydroxide at 60 °C. After dialyzing the reaction mixture, amine groups were introduced on the surface of CNC by opening the epoxide rings using ammonium hydroxide at 60 °C. The final product was obtained after dialysis until a pH of 7.[10] In another study, amine groups were introduced on the surface of CNC by esterification and consecutive thiol-ene click reaction.[11] Click-chemistry was also applied to prepare amine functionalized CNC. Firstly, azide groups were introduced to the surface of CNC via etherification of 1-azido-2,3-epoxy- propane in a mixture of isopropanol/basic water at room temperature. In the next step, pH-responsive amine decorated CNC was achieved by reacting the azide groups with propargyl amine via copper catalyzed azide-alkyne cycloaddition.[12] In a recent study, amine functionalized CNC was obtained via a two-step procedure in aqueous media at ambient temperature. In the first step, the primary hydroxyl groups on the surface of CNC were converted to carboxylic acid via TEMPO-mediated oxidation. In the next step, peptidic coupling reaction between carboxylic acids and amines on bifunctional amines of small alkyl chain length was conducted.[4] Amine groups have also been introduced on the surface of CNC by grafting with chitosan oligosaccharide.[13]

In this study, we develop and optimize the functionalization of CNC with primary amines in aqueous solution in a simple reaction protocol. The synthetic protocols previously used for the synthesis of amine functionalized CNC was modified and different reaction parameters, such as time, temperature, ratios of CNC and reagents, and the effect of reflux were optimized leading to a higher content of surface amine groups. The pH-responsive properties of amine functionalized CNC was investigated by viscosity measurements. We also investigated one of the potential applications of amine CNC as a flocculating agent in water treatment by interacting it with a negatively charged surfactant.

2. Experimental

2.1. Materials

Spray-dried cellulose nanocrystal (CNC) sample was supplied by Celluforce Inc. Epichlorohydrin (EPH), dimethylsulfoxide (DMSO), tetrabutylammonium hydroxide (TBAH), sodium dodecylsulfate (99%) (SDS) were purchased from Sigma–Aldrich. Ammonium hydroxide (28–30% NH_3 in water) was purchased from Acros organics. Millipore de-ionized (D.I.) water was used for all experiments and sample preparations.

2.2. Synthesis and optimization of amine functionalized cellulose nanocrystals

In the first step, epichlorohydrin (1.46 ml) was added to ammonium hydroxide (3.78 ml) and heated to 65 °C for 2 h. In the second step, CNC (1.00 g) was dispersed in DMSO (66.66 ml) and different amounts of TBAH were added to the mixture in a round bottom flask (molar ratio of TBAH/AGU: 0.1-1.0). Contents from the reaction in step 1 were removed using a syringe and added to the second mixture in a drop-wise manner. The reaction mixture was stirred for various time intervals (0.5–8 h) and heated at different temperatures (25–85 °C) for studies on determining the optimal reaction conditions. The reaction mixture was purified by dialysis (M_W cut off: 12,000 g/mol) against D.I. water for at least one week until the conductivity of the dialysis medium remained constant yielding a final product designated as CNC–NH_2(T). Further purification of the reaction mixture was obtained by lowering the pH to ~2, which induced the agglomeration of amine CNC nanoparticles between positive NH_3^+ and negative OSO_3^- groups. The agglomerated amine CNC was separated by centrifugation at 10,000 rpm for 1 h. The sediment was redispersed in an alkaline aqueous solution, and the process was repeated once, where the purified product comprised of the sediment (CNC–NH_2(P)) and supernatant (POLY–NH_2).

2.3. Potentiometric titration

The amine content of the amine functionalized CNC was determined by potentiometric titration. A Metrohm 809 Titando automatic titrator was used and the pH and conductivity were measured simultaneously. The titrator is equipped with a Tiamo software that doses μL of titrants. All measurements were performed in a closed jacketed vessel at 25 °C and the stirrer was set at a medium rate. 50 ml of 0.1 wt % CNC suspension were prepared in D.I. water. The pH of the suspension was adjusted to ~3 using 1 M HCl. In order to remove the dissolved CO_2 and avoid the formation of carbonic acid, the purified amine CNC suspension was degassed by bubbling argon gas into the solution. The suspensions were titrated using 0.1 M NaOH under argon blanket and stirring. The conductivity and pH of the suspensions were measured simultaneously until the pH of the samples approached ~11. Finally, the pH and conductivity values were plotted against the volume of NaOH (in mL), which were used to determine the content of amine groups.

2.4. FTIR

FTIR spectra of the dried KBr pellets of pristine CNC, CNC–NH_2(T), CNC–NH_2(P), and POLY–NH_2 were determined using a Bruker Tensor 27 spectrometer with resolution of 4 cm^{-1} and a number of scans of 32 from 400 to 4000 cm^{-1}. KBr pellets were prepared by grinding approximately 2% of the samples in KBr and compressed into a pellet. The FTIR Spectra were monitored and analyzed using the OPUS software.

2.5. Elemental analysis

The percent of carbon (C), hydrogen (H), nitrogen (N) and sulfur (S) contents (%) of pristine CNC, CNC–NH_2(T), CNC–NH_2(P) and POLY–NH_2 were determined by a CHNS, Vario Micro Cube, Elemental Analyzer. The freeze-dried samples were combusted at 1000 °C and the combustion products were detected by a thermal conductivity detector for quantitative analysis.

2.6. TEM

Transmission electron microscopic (TEM) images of pristine CNC, CNC–NH_2(T), and CNC–NH_2(P), were recorded using a Philips CM10 TEM with 60 keV acceleration voltages. Approximately 10 μL of 0.01 wt % aqueous suspensions of the samples were deposited on a carbon-formvar film on 200 mesh copper grids. In order to minimize possible agglomeration of the particles, excess solvent was removed from the grids placed on a filter paper. Then the grids were allowed to dry over night.