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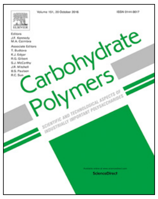

Disk-like nanocrystals prepared by solvolysis from regenerated cellulose and colloid properties of their hydrosols

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ABSTRACT

One possible way of obtaining cellulose nanocrystals and aqueous sols with novel properties is based on modification of supramolecular structure of the polysaccharide. This modification involves rearrangements of hydrogen bonds and has an effect on polymer morphology, formation of surface reactive sites and interface interactions. Disc-like nanocrystals of cellulose II were prepared by solvolysis of regenerated cellulose in acetic acid/octanol medium in the presence of 0.4 mol% of phosphotungstic acid. The starting cellulose samples were dissolved and regenerated in the NaOH/thiourea system. Cellulose nanocrystals were studied by transmission electron microscopy, atomic force microscopy, dynamic light scattering, FTIR spectroscopy, XRD and thermogravimetric analysis. Colloidal stability of aqueous suspensions of cellulose nanocrystals in the presence of electrolyte (KCl) was studied. Their acid-base properties were revealed using potentiometric titration. The influence of electrolyte concentration on dynamic viscosity of the obtained hydrosols and their ability to show birefringence was established.

1. Introduction

Due to their ordered structure, nanocrystals demonstrate constancy of properties in time, relatively high chemical resistance and stability against multifactor effects. Organic nanocrystals are distinguished by certain flexibility of organic molecules and ability for rearrangement; in addition, it is possible to apply organic chemistry tools for modification of their surface.

The most familiar examples of organic nanoparticles with ordered structure are polymeric and, particularly, polysaccharide nanoparticles (Lin, Huang, & Dufresne, 2012). Among the latter group, cellulose nanocrystals (CNC) have been most actively studied. Ultrafine particles and the systems based on these particles combine specific properties that are inherent to the materials with small morphological elements (less than 100 nm in size) and such characteristics as availability, ordered structure, possibility of surface modification (Eyley & Thielemans, 2014; Zoppe et al., 2014). This modification can be carried out with the aid of carbohydrate chemistry methods, by casting films, making filaments, preparation of structured colloidal systems (Araki & Kuga, 2001; Habibi, Lucia, & Rojas, 2010). Besides, cellulose nanocrystals are biocompatible and environmentally-safe materials (Grishkewich, Mohammed, Tang, & Tam, 2017).

In the past decade, numerous ways for obtaining CNC have been proposed. The most widely used methods include hydrolysis catalyzed by sulfuric acid or hydrohalic acids (Liu et al., 2016; Sadeghifar, Filpponen, Clarke, Brougham, & Argyropoulos, 2011), mechanochemical, oxidative or biotechnological methods (Postek, Moon, Rudie, & Bilodeau, 2013). Application of heteropolyacids in CNC preparation involving various additional techniques and components has been reported (Hamid, Zain, Das, & Centi, 2016; Liu et al., 2014;

Abbreviations: AGU, anhydroglucose unit of cellulose; CS, microcrystalline cellulose; CR, regenerated cellulose; CNC, cellulose nanocrystals; CNC_R, cellulose nanocrystals recovered; PTA, Phosphotungstic acid; TEM, Transmission electron microscopic; DLS, dynamic light scattering; XRD, X-ray diffraction; IC, index of crystallinity; D(hkl), size of crystallites; FTIR, Fourier transform infrared spectra; TGA, thermogravimetric analyses; AFM, atomic force microscope; T_{fin}, final temperature of cellulose thermal degradation; T_{st}, starting temperature of cellulose thermal degradation; T_{max}, temperature of maximum rate of thermal degradation; d_h, hydrodynamic diameter of CNC; ΔA, change in optical density; W, experimental stability factor

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Torlopov et al., 2018). As a rule, direct use of all these methods results in the nanocrystals with supramolecular structure typical of the initial natural polymer (the so-called cellulose I) (Nugmanov, Pertsin, Zabelin, & Marchenko, 1987). The prepared nanocrystals have rod-like morphology. Certain specific techniques (e.g., selection of a cellulose precursor, use of ultrasound or biotechnological methods) allow the preparation of particles with crystalline structure of cellulose I, but with different morphology (Satyamurthy & Vigneshwaran, 2013; Xiong, Zhang, Tian, Zhou, & Lu, 2012).

A distinguishing feature of cellulose crystalline domains is their ability to undergo polymorphic transition. The natural cellulose (polymorph I) can be used for obtaining other modifications, the so-called celluloses II and III (Ciolacu & Popa, 2011). Polymorphic transition is accompanied by changes in the structure of intra- and intermolecular hydrogen bonds, crystallite shape and size. These changes inevitably affect chemical and physical parameters of nanoparticle surface, morphology, interactions at interfacial boundary. Thus, polymorphic transition offers interesting prospects of obtaining cellulose nanocrystals and sols with new colloid-chemical properties. First of all, these considerations apply to colloidal stability of hydrosols of cellulose nanocrystals, ability to form mesophases, and rheological characteristics of colloidal systems that depend both on particle morphology and structure of interfacial boundary.

Cellulose with polymorphic modification II is prepared by regeneration of natural cellulose from solutions or by alkali treatment of raw material. Cellulose can be dissolved in various mixtures, particularly, in aqueous solutions of sodium hydroxide and urea (Jin, Zha, & Gu, 2007). The main distinguishing feature of cellulose II is a specific system of intermolecular hydrogen bonds that differs from the corresponding system in cellulose I and, as a rule, imparts higher stability to polymorph II (Langan, Nishiyama, & Chanzy, 2001; Nugmanov et al., 1987).

Cellulose with crystalline structure II was used in preparation of nanoparticles with different morphologies. After preliminary alkali treatment, mercerized cotton fibers were subjected to incomplete hydrolysis in aqueous solution of sulfuric acid. This process gave rod-like particles with higher thermostability than that of cellulose I particles; their hydrosols had higher viscosity as compared with the viscosity of cellulose I hydrosols of similar concentration (Yue et al., 2012). Rod-like nanocrystals of cellulose II were also obtained by oxidation of mercerized cellulose (Hirota, Tamura, Saito, & Isogai, 2010), and by mercerization of nanocrystals prepared in the process of acidic hydrolysis (Jin et al., 2016). Cellulose II nanocrystals with ribbon-shape morphology were produced in solutions of sulfuric acid as a result of the corresponding rearrangement in cellulose I structure (Sèbe, Ham-Pichavant, Ibarboure, Koffi, & Tingaut, 2012).

Spherical particles of cellulose II were prepared by hydrolysis of mercerized cellulose isolated from flax stems; the process was carried out in solution of sulfuric acid (Astruc et al., 2017). Spherical nanoparticles 30 nm in diameter were also obtained after hydrolysis of regenerated cellulose in the formic acid/HCl mixture; the process involved esterification reaction between surface hydroxyl groups of cellulose nanoparticles and carboxyl groups of HCOOH (Yan, Yu, & Yao, 2015).

Cellulose regenerated after dissolving in organic medium was hydrolyzed in the mixture containing ammonium persulfate (Cheng et al., 2014). The prolonged treatment of regenerated cellulose (for several hours) at elevated temperatures resulted in the formation of plate-like particles enriched in carboxyl groups.

To summarize, several methods for obtaining cellulose nanocrystals with various morphologies have been described in the literature so far. At the same time, only fragmentary and incomplete information about the influence of polysaccharide supramolecular structure on CNC properties can be found. There are few available data on colloid-chemical properties of CNC-containing dispersions, but the studies in this field are greatly complicated by strong dependence of CNC properties on various factors (preparation method, pretreatment technology, type of cellulose material). Almost all methods lead to certain functionalization of nanoparticle surface. Therefore, in order to reveal the overall trends in CNC dispersions, it is necessary to conduct systematic and detailed studies of preparation and characteristics of cellulose nanocrystals with various polymorphic modifications, and to investigate their dispersions.

Previously, we have proposed the method for controlled solvolysis of cellulose with the use of CH_3COOH/octanol-1 mixture in the presence of phosphotungstic acid (Torlopov et al., 2018). In the rod-like nanocrystals prepared by this method, chemical and supramolecular structure of native cellulose is little affected. The present work is a systematic development of the earlier studies and focuses on preparation of CNC with cellulose II polymorph. Special attention is given to the most important colloid-chemical properties of sols obtained from these particles.

2. Experimental

2.1. Materials

Cotton microcrystalline cellulose (further named CS) was provided by “Polyex” (Biysk, Russia) and was used as a starting cellulose material. Its degree of polymerization was 220 (determined by viscometry in cadoxen solution), and the content of α-cellulose was 99.8%. Phosphotungstic acid ($H_3PW_{12}O_{40}$, PTA), acetic acid, sulfuric acid, octanol-1, ethanol (reagent grade) were purchased from “Vekton” (Russia), and hydrogen peroxide (35% w/w aq.sol.) was purchased from “AlfaAesar”. Working solutions were prepared immediately before experiments.

2.2. Methods

Preparation of regenerated cellulose (further named CR) was carried out using the NaOH/thiourea system; the method described by Jiang et al. (2017) was slightly modified. Briefly, 30.0 g of CS was introduced portion wise at stirring into the cooled (down to 5 °C) solution that contained 47.5 g of NaOH, 22.5 g of thiourea and 450 mL of water. The obtained suspension was cooled down to −12 °C. At this temperature, complete dissolution was reached in 4 h. To isolate cellulose, the solution was transferred to 3 liters of water. The resulting mixture was neutralized while stirring and cooling by carefully adding 30% (v / v) H_2SO_4 until pH 5. The cellulose flakes were separated, washed with water until a neutral pH of wash water and then freeze-dried.

Preparation of CNC, optimized technique. Catalytic solvolysis of cellulose was carried out in the CH_3COOH/octanol-1 mixture (volume ratio 1:9) in the presence of PTA. Preliminary studies revealed the possibility of using this system in preparation of the CR-based nanoparticles. The optimized ratio between the components of the mixture (CH_3COOH/octanol = 9:1 v/v) was taken as a basic composition. CR dried to constant weight at 105 °C (5.0 g, 30.9 mmol of cellulose anhydroglucose unit - AGU) was placed into a round-bottom flask equipped with thermometer, reflux condenser and stirrer; then, acetic acid (45 mL) was added. The mixture was heated up to 117 °C and exposed at this temperature for 60 min. PTA solution was prepared separately. PTA (0.356 g, 0.124 mmol, 0.40 mol% with respect to AGU) was dissolved in 5.0 mL of octanol-1. The resulting PTA solution was introduced into CH_3COOH/CR suspension, and the mixture was stirred at 114 °C. The reaction mixture darkened in several minutes after addition of PTA. In order to provide decolorization and restore catalyst activity, 50 μL of hydrogen peroxide was added, and then, the same amount of oxidant was added every 5 min. The total reaction time was 60 min.

After reaching the reaction time required, the reaction was stopped by quenching the reactor in an ice-cool water bath; the precipitate was separated by centrifugation (2000 RCF, 5 min). The obtained