



Preparation of fungus-derived chitin nanocrystals and their dispersion stability evaluation in aqueous media



Ning Lin^{b,1}, Shasha Zhao^{b,1}, Lin Gan^{a,1}, Peter R. Chang^c, Tao Xia^b, Jin Huang^{a,b,*}

^a School of Chemistry and Chemical Engineering, Joint International Research Laboratory of Biomass-Based Macromolecular Chemistry and Materials, Southwest University, Chongqing 400715, China

^b School of Chemistry, Chemical Engineering and Life Sciences, Wuhan University of Technology, Wuhan 430070, China

^c Bioproducts and Bioprocesses National Science Program, Agriculture and Agri-Food Canada, 107 Science Place, Saskatoon, Saskatchewan S7N 0X2, Canada

ARTICLE INFO

Article history:

Received 15 January 2017

Received in revised form 6 May 2017

Accepted 5 June 2017

Available online 10 June 2017

PACS:

PACS

75.40.-s

71.20.LP

Keywords:

Chitin nanocrystals

Mushroom

Dispersion stability

Critical aggregation concentration

DLVO theory

ABSTRACT

The chitin nanocrystal is a promising nano-reinforcing agent, but the parasitic pathogens carried on crabs and shrimp shells as main sources limit its application in some fields. In this study, the ChNs which avoided possible safety risks were extracted from mushrooms via protein/mineral-purification and subsequent HCl-hydrolysis. Such fungus-derived ChNs presented an α -chitin crystalline structure with a length of 143 ± 24 nm and a diameter of 10 ± 2 nm. Since the dispersion stability of ChNs suspension determines their further applications, this present study emphasized the dispersity of ChNs in aqueous media evaluated by the viscosity under steady-shear flow and UV-vis absorption, whose results indicated that ChNs in dispersion would aggregate when the concentration of homogeneous dispersion reached 0.5–0.6 wt%. To explore the effect of electrostatic repulsion on interactions between nanoparticles, the maximum energy barriers for parallel and crossed orientations of ChNs in suspension were analyzed using a traditional DLVO theory with additions of NaCl solutions.

Crown Copyright © 2017 Published by Elsevier Ltd. All rights reserved.

1. Introduction

Chitin is the second most abundant linear polysaccharide consisting of $\beta(1-4)$ linked *N*-acetyl-D-glucosamine units (Möller, Grelier, Pardon & Coma, 2004), which can be found as a major component in shells of arthropods, backbones of squids and insects, as well as cell walls of some fungus (Majtán et al., 2007; Vetter, 2007; Wu, Zhang, Girouard & Meredith, 2014). Isolated from chitin fibers, the highly-crystalline and rigid chitin nanocrystals possess numerous outstanding properties including low cost, environmental friendliness, renewability, biodegradability and nontoxicity, which promote widely researches and applications in composites, water treatment, cosmetics, medical and pharmaceutical fields (Zeng, He, Li & Wang, 2012). Besides, due to the high surface area and longitudinal modulus (150 GPa) (Huang et al., 2015), chitin nanocrystal is a promising nano-reinforcing agent to enhance the

mechanical properties of polymers, such as poly(caprolactone) (Morin & Dufresne, 2002), natural rubber (Nair, Dufresne, Gandini & Belgacem, 2003), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (Wang et al., 2012), starch (Salaberría, Labidi & Fernandes, 2014), chitosan (Naseri et al., 2014), alginate (Huang et al., 2015) and poly(vinylidene fluoride) (Qin, Li, Zhao, Liu & He, 2015), polyethylene (An et al., 2016). Moreover, chitin nanocrystals have been reported in the developments of functional materials as hydrogel (Nikiforidis & Scholten, 2015), bioscaffold (Liu et al., 2016), emulsion stabilizer (Tzoumaki, Karefyllakis, Moschakis, Biliaderis & Scholten, 2015; Tzoumaki, Moschakis, Kiosseoglou & Biliaderis, 2011), water filtration membrane (Goetz, Jalvo, Rosal & Mathew, 2016), shape-memory bionanocomposites (Saralegi et al., 2013), biorecognitive fluorophores (Zhou et al., 2014) and antifungal materials (Robles, Salaberría, Herrera, Fernandes & Labidi, 2016).

Chitin nanocrystals are generally extracted from crustacean wastes, crab (Ifuku et al., 2009; Muzzarelli, El Mehtedi, & Mattioli-belmonte, 2014) and shrimp shells (Goodrich & Winter, 2007). Unfortunately, despite of the fruitful source of crustacean wastes, the quality of chitin resources was greatly influenced by the seasonal factors and geographical differences (Di, Rapanà, Tomati & Galli, 2008). In chitin-derived animal resources, the high contents of impurities involving calcium carbonate, proteins, pigments, lipids

* Corresponding author at: School of Chemistry and Chemical Engineering, Joint International Research Laboratory of Biomass-Based Macromolecular Chemistry and Materials, Southwest University, Chongqing 400715, China.

E-mail addresses: huangjin@iccas.ac.cn, huangjin2015@swu.edu.cn (J. Huang).

¹ These authors contributed equally.

and minerals may result in tedious purification treatments and possible structural changes of chitin during the processes (Salaberría, Labidi & Fernandes, 2014). Furthermore, parasitic pathogens were commonly carried on crabs (Kroft & Blakeslee, 2016) and shrimp shells (Tang et al., 2015), which indeed were potential risks to the health of experimenters (Thitamadee et al., 2016). Therefore, explorations of new chitin resources with stable, eco-friendly and safe advantages for preparation of chitin nanocrystals are still meaningful and imperative.

Meanwhile, the processing of nanoparticles is generally associated with dispersion or aggregation in solvent to form colloidal suspensions, which requires a stable and homogeneous dispersion when serious aggregation should be avoided in suspensions. Rod-shaped nanoparticles are reported with random dispersion and orientation in the suspension, exhibiting the special behaviours of birefringence, liquid crystalline, phase separation, and thixotropy (Boluk, Zhao & Incani, 2012). With regard to the rod-like chitin nanocrystals in aqueous suspension, they would preserve a stable dispersion state in water at pH 3–4 due to the presence of amino groups on surface of nanocrystals (Fan, Saito & Isogai, 2010). In fact, the protonation effect of amino groups in acidic condition provides a necessary electrostatic repulsion for homogeneous dispersion of chitin nanocrystals in aqueous suspension, which might further promote the subsequent processing in composites, cosmetics, food and biomedical materials. For example, the initial dispersion state of chitin nanocrystals in suspension probably affect that in chitin nanocrystal reinforced composites, which would directly determine the interfacial interaction, microstructure and mechanical properties of obtained composites (Araki & Kurihara, 2015). Even for the basic microscopy observation of morphology, the well-dispersed state of nano particles in suspension was demanded, which may be promoted by the ultrasonic treatment before the observation (Shafiei-Sabet, Hamad & Hatzikiriakos, 2012). Recently, chemical modification was performed with surficial grafting poly (ethylene glycol) to enhance the steric repulsion and improve the dispersion stability of chitin nanocrystals in suspension (Araki & Kurihara, 2015). However, due to the lack of standards for the dispersion states and quantification for the attractive or repulsive forces between nanoparticles, rare of studies about the critical concentration of chitin nanocrystals, or nanocelluloses, and mechanism discussions on the electrostatic repulsion for the stable dispersion in suspension have been reported.

In order to solve the problems above, a non parasitic pathogens source is necessary for preparation of chitin nanocrystals, the critical concentration of which for stable dispersion in suspensions should be studied as well. Thus, in the present study, we choose a fungus source of mushroom to extract chitin and isolate chitin nanocrystals. Then, the crystallinity, thermal stability and morphology of chitin nanocrystals obtained from mushroom were studied by X-ray diffraction (XRD), thermo gravimetric analysis (TGA) and transmission electron microscope (TEM). Besides, the dispersion stability of chitin nanocrystals in aqueous suspensions with different concentrations were characterized by the birefringence observation and Tyndall scattering test, and Ultraviolet–visible spectroscopy and rheological tests. Finally, the mechanism on electrical double layer related to the electrostatic repulsion for the stable dispersion of chitin nanocrystals were discussed on the basis of DLVO theory.

2. Materials and methods

2.1. Materials

The mushrooms (*Tricholoma gambosum*) used in this study were commercially available from Wuhan Westeast Lake Edible

Fungus Business Co. Ltd. (China). Sodium hydroxide, hydrochloric acid (37%, w/w), hydrogen peroxide (30%, w/w) were all analytical-grade reagents and purchased from Shanghai Sinopharm Chemical Reagent Co. Ltd. (China).

2.2. Preparation of chitin nanocrystals from mushrooms

The chitin nanocrystals were extracted from mushrooms in a way similar to that from crab shell, which included two process: the purification treatment and acid hydrolysis (Wijesena et al., 2015; Ifuku et al., 2009). The raw materials were thoroughly grinded, and the small particles of each material were sifted through a 200-mesh sieve. Then the powders were dispersed into an aqueous solution of 2 wt% sodium hydroxide by vigorous stirring at 80 °C. In order to remove the soluble impurities, the treated suspension was washed with water for three times by centrifugation and then bleached with a solution of 5 wt% hydrogen peroxide at 80 °C, followed by centrifugation and dispersion in distilled water for three times. The obtained suspension was treated with another aqueous solution of 2 wt% sodium hydroxide for 48 h at room temperature to further remove the proteins and minerals. The obtained produce (raw chitin) was washed and dialyzed with distilled water until the pH was between 5 and 6. The purified chitin was hydrolyzed with a solution of 3 M HCl (hydrochloric acid was used to avoid grafting charged groups) (Tang, Lv, Xu, Tan & Dong, 2016; Wijesena et al., 2015) at 105 °C for 1.5 h under the magnetic stirring. Then, the suspension was washed and centrifuged with distilled water, followed by dialysis of five days. Finally, in consideration of necessity of solid state chitin nanocrystals for conventional processing of reinforced composites based on them, the white and loose powders of chitin nanocrystals were released from suspension via the freeze-drying treatment (Shanghai boyikang Laboratory Instrument Co. Ltd.), the yield of chitin nanocrystal is about 2 wt%. The procedure was shown in Fig. 1.

2.3. Stability evaluation

The dispersion stability of chitin nanocrystals in aqueous suspension was characterized via three methods, such as the observation of flow birefringence and Tyndall scattering phenomenon, measurement of UV–vis absorption and viscosity analysis of suspension with different concentrations of chitin nanocrystals. Firstly, in the observation part, an aqueous suspension (0.05 wt%) of chitin nanocrystals was fixed between two polarizing films in a dark room after ultrasonic treatment, and a light source was placed behind each film for flow birefringence observation of the suspension. The Tyndall scattering of chitin nanocrystal suspension (0.05 wt%) which was related to the particle size and the incident wavelength was observed in a dark room with a green light source at one side of the suspension.

In the UV–vis part, Since the self-aggregation of chitin nanocrystals in suspension might induce the decrease of UV–vis absorption value, the UV–vis absorption measurement was performed on chitin nanocrystal suspensions (50 mL) with different concentrations between 0.005 and 1 wt% by using a UV–vis spectrometer (UV-2600, Shimadzu, Japan). Besides, all suspensions were stored under room temperature for 7 d, in which their UV–vis absorption was measured for several times.

In the viscosity analysis part, the shear viscosity, another parameter reflecting the dispersion state of chitin nanocrystals in aqueous suspension, was measured via a Thermo Scientific HAAKE RheoStress 600 Rheometer (Thermo Electron Corporation, Germany) equipped with a DG 41-Ti cup. The measurement was performed for suspensions with different concentrations (from 0.1 to 1.5 wt%) at room temperature, and the shearing rates were varied from 0.01 to 100 s⁻¹.

Download English Version:

<https://daneshyari.com/en/article/5157438>

Download Persian Version:

<https://daneshyari.com/article/5157438>

[Daneshyari.com](https://daneshyari.com)