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Understanding shape and morphology of unusual tubular starch nanocrystals

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ABSTRACT

Starch nanocrystals (SNC) are aptly described as the insoluble degradation byproducts of starch granules that purportedly display morphologies that are platelet-like, round, square, and oval-like. In this work, we reported the preparation of SNC with unprecedented tubular structures through sulfuric acid hydrolysis of normal maize starch, subsequent exposure to ammonia and relaxation at 4 °C. High-resolution transmission electron microscopy observation clearly proved that the SNCs possess tubular nanostructures with polygonal cross-section. After further reviewing the transformations of SNC by acid hydrolysis, ammonia treatment, and curing time at 4 °C, a mechanism for T-SNC formation is suggested. It is conjectured that T-SNC gradually self-assembles by combination of smaller platelet-like/square nanocrystals likely loosely aggregated by starch molecular chains from residual amorphous regions. This work paves the way for the pursuit of new approaches for the preparation of starch-based nanomaterials possessing unique morphologies.

1. Introduction

Native starch (amylose/amylopectin) is a complex polysaccharide biosynthesized by tracheophytes (vascularized plants) as their primary energy store that also serves as the major food source for human beings and animals. It is ubiquitous, biodegradable, biocompatible, and non-toxic (Dufresne, 2006; Le Corre, Bras, & Dufresne, 2010), and has consequently attracted significant attention as a green biopolymer feedstock over the last two decades. Native starches possess discrete and partially crystalline granular segments having dimensions ranging from 1 to 100 μm (Tester, Karkalas, & Qi, 2004; Zhang, Zhou, Lian, & Wu, 2013).

Generally, starch is a heterogeneous composite of two polyglucans, i.e., amylose and amylopectin, both of which are characterized by α-linked D-glucosyl units (Buléon, Colonna, Planchot, & Ball, 1998; Gallant, Bouchet, & Baldwin, 1997; Parker & Ring, 2001). Amylose is a linear polymer able to react with iodine, organic acids, and alcohols via helical inclusion complexes that possess a hydrophobic internal surface, a system termed "spiral clathrate". Amylopectin is a highly branched polymer characterized by a cluster of amylopectin side chains which provide the partial crystallinity of native starch granules. Starch granules exhibit a nominal onion-like structure with nearly concentric growth rings (Putaux, Molina-Boisseau, Momaur, & Dufresne, 2003). The growth rings correspond to concentric semi-crystalline shells with a thickness of 120–500 nm, separated by amorphous regions (Dufresne, 2014; Kim, Park, & Lim, 2015). The semi-crystalline regions consist of amorphous and crystalline lamellae with a distance of 9–10 nm, which contain amylopectin's and amylose's molecular structure of 0.1–1 nm (Jenkins, Cameron, & Donald, 1993; Jenkins & Donald, 1995, 1997; Waigh, Donald, Heidelbach, Riekel, & Gidley, 1999).

The amorphous lamellae of starch granules are usually not as impervious to chemicals as their crystalline lamellae counterparts. The acid hydrolytic disruption of the amorphous and semi-crystalline lamellae results in the enrichment of the crystalline lamellae to provide a functional nanoparticle known as

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starch nanocrystals (SNC) (Dufresne, 2014; Kim et al., 2015). The SNC were first observed by Putaux et al. (2003) after treating waxy maize starch granules with 2.2 N HCl at 36 °C for 2 weeks. They possess the morphology of crystalline platelets with a length of 20–40 nm, a width of 15–30 nm, and a thickness of 5–7 nm (Putaux et al., 2003). A short time later, Angellier, Choisnard, Molina-Boisseau, Ozil, and Dufresne (2004) reported that a similarly shaped SNC could be obtained by using 3.16 M H_2SO_4 to hydrolyze waxy maize starch granules at 40 °C at a starch concentration of 14.69 wt-%; the reaction time can be shortened to 5 days. Consequently, both HCl and H_2SO_4 have been the widely used mineral acids for the preparation of SNC (Namazi & Dadkhah, 2008; Jin et al., 2015; Wang, Yu, Jin, & Yu, 2008; Wei, Li, Tian, Xu, & Jin, 2015; Wei et al., 2016). The resultant platelet morphology of SNC prepared from waxy maize starch granules has been observed and widely accepted (Angellier-Coussy et al., 2009; Dufresne, 2014; Haaj, Thielemans, Magnin, & Boufi, 2016; Le Corre & Angellier-Coussy, 2014).

Le Corre, Bras, and Dufresne (2011) investigated the influence of botanic origin and amylose content on the morphologies of SNC. It was found that the amylose content and crystalline type are more influential on the SNC morphology than the botanic origin. The morphology of SNC produced from A-type starches such as waxy maize and wheat starches is square-like, whereas that produced from B-type starches such as potato starch and high amylose starch displays disk-like platelets. In general, it has been found that maize SNC is expressed as round- and square-like platelet particles (Le Corre et al., 2011). García, Ribba, Dufresne, Aranguren, and Goyanes (2011) were able to generate grape-like SNC by H_2SO_4 hydrolysis of waxy maize starch granules. Kim, Lee, Kim, Lim, and Lim (2012) discovered that the starch fragments generated by acid hydrolysis are expressed in spheroidal or ovaloid shapes regardless of starch origins, a finding that is contrary to the platelet-like structures reported previously. Sonthanasamy, Ahmad, Fazry, Hassan, and Lazim (2016) prepared round or oval crystalline starch nanoparticles with diameters ranging from 50 nm to 90 nm by acid hydrolysis of Gadong starch, which corroborated Kim et al.'s discovery (2012). However, to the best of our knowledge, no tubular starch nanocrystals (T-SNC) have been reported.

The importance of starch as a polysaccharide feedstock is overwhelming. Its derivative, SNCs, for example, have shown potential applications ranging as reinforcing agents in natural rubber (Angellier, Molina-Boisseau, Lebrun, & Dufresne, 2005) or in the other bio-sourced/bio-degradable polymers (Condés, Añón, Mauri, & Dufresne, 2015; Duan, Sun, Wang, & Yang, 2011; Espino-Pérez et al., 2016; García et al., 2011; Li et al., 2015), emulsion particle stabilizers (Haaj, Thielemans, Magnin, & Boufi, 2014; Li, Sun, & Yang, 2012), adsorbents for the removal of pollutants (Alila, Aloulou, Thielemans, & Boufi, 2011), matrices to support expensive metal catalysts (Verma, Bras, Jain, & Muzart, 2013; Verma, Tripathi et al., 2013), and controlled drug release carriers (Lin, Huang, Chang, Feng, & Yu, 2011; Xiao et al., 2016). What must be appreciated, however, is that these applications are heavily related to the respective morphology of the as-prepared SNCs. Therefore, efforts to reveal and/or control the factors responsible for the morphologies of SNC are highly critical.

Thus, in this work, T-SNCs were prepared by sulfuric acid hydrolysis of maize starch granules that was proceeded by treatment with ammonia and relaxation at 4 °C. The formation process was uncovered by systematically analyzing the variations in the SNCs with respect to acid hydrolysis, ammonia treatment, and relaxation time at 4 °C. Remarkably, it was determined that the SNCs are composed of tubular structures of varying degrees of polygonal morphologies although from a gross perspective they are spheroidal or ovaloid under SEM or before ammonia treatment under TEM. It is proposed that the tubular SNCs are arranged by a re-combination of smaller platelet-like/square nanocrystals loosely connected by flexible starch chains of residual amorphous regions due to a singular relaxation phenomenon at 4 °C over 5 days. This unique discovery provides a new approach for preparing starch-based nanomaterials displaying interesting morphologies for potential application in drug delivery.

2. Experimental

2.1. Materials

Normal maize starch was kindly provided as white powder with a purity greater than 99.5 wt-% (based on oven-dry starch) by Yanzhou Xilai Fine Chemistry Co., Ltd. (Shandong, China). Sulfuric acid, ammonia ($NH_3 \cdot H_2O$, 25–30 wt-%), hydrochloric acid, sodium hydroxide, and other chemicals were all of analytical grade and used without further purification. Deionized water was used throughout the experiment and prepared by ion exchange.

2.2. Preparation and characterization

Normal starch nanocrystals (SNC) were prepared by H_2SO_4 hydrolysis of native maize starch granules (Angellier et al., 2004; García et al., 2011). In a typical process, normal native maize starch granules (36.72 g) were dispersed in 250 mL of 3.16 M H_2SO_4 solution, the mixed suspension was warmed to 40 °C, and magnetically stirred for 7 days at 100 rpm. The resultant suspension was centrifuged at 4500 rpm and washed with deionized water until the supernatant was pH 5 to obtain normal SNCs. The centrifuged cake was further treated by 1 wt-% ammonia for 20 min. After the supernatant of SNC-ammonia dispersion was separated by centrifugation at 4500 rpm for 20 min, the precipitate, i.e., the obtained ammonia-treated SNC was washed by successive centrifugation at 4500 rpm with distilled water until pH 9. Afterwards, the sample relaxed for a pre-set time at 4 °C. Part of the relaxed sample was freeze-dried and labeled as dried T-SNC, which was used for scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier-transform infrared (FT-IR), and X-ray photoelectron spectroscopy analyses. The leftover sample was diluted with deionized water to 10 wt-%, forming a T-SNC dispersion, which was subjected to transmission electron microscopy (TEM) analysis. The supernatant from the SNC-ammonia dispersion was centrifuged at 10,000 rpm for 5 min. The obtained secondary precipitate was used to analyze the ammonia-removed component by TEM. SEM images were used to characterize the morphology and size of the as-prepared T-SNC, obtained with a HITACHI S-4800 field-emission scanning electron microscope (FE-SEM) and compared with that of native maize starch granules and SNCs after the dried SNC, T-SNC, and starch granules were attached to conductive tape and coated by Au. The morphology and structural details of SNCs, T-SNCs, and components removed from SNC by ammonia treatment were also analyzed by a JEOL JEM 2100F high-resolution transmission electron microscopy (HR-TEM), in which the sample was prepared by dripping a drop of dilute sample dispersion on a TEM ultra-thin carbon supporting film. FT-IR spectra were used to analyze functional groups of the as-prepared SNC samples as performed on a Nicolet Avatar 370 infrared spectrometer in the range of 400–4000 cm^{-1} using pressed KBr discs. XPS spectra were used to analyze the chemical composition of the as-prepared SNC samples, and recorded on an ESCALAB 250 photoelectron spectrometer. Water contact angle was measured to characterize the water-wettability of starch and SNC samples (Kushwaha, Avadhani, & Singh, 2015). Deionized water was used in contact angle measurements. The contact angle was measured using an optical contact angle measuring device (JC2000C1, Shanghai Powereach Co., Ltd.) after the starch/SNC samples were compressed into