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Eco-friendly isolation of cellulose nanoplatelets through oxidation under mild conditions

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ABSTRACT

Agave is recognized as a low recalcitrant material, which makes it a potential source to obtain nanocellulose. Aqueous dispersions (in water, H_2O_2, H_2O_2/H_2SO_4) of agave powder were heated at 120 °C under vapor pressure (1 kg/cm^2). The resultant materials were observed with an optical microscope (OM), a laser scanning microscope (LSM) to obtain the thickness measurement and a scanning electron microscope (SEM) to observe morphology. Raman spectroscopy, X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) were used to obtain the chemical structure. Cellulose nanoplatelets (CNPs) from *Agave salmiana* were successfully isolated under mild conditions. Physicochemical analysis indicates that lignin was removed in a single step oxidation with hydrogen peroxide in presence of sulfuric acid at low concentration (0.17 M). The CNPs images revealed the presence of entangled cellulose nanofibrils (Ø ≈ 14 nm) along the nanoplatelets (thickness ≈80 nm).

1. Introduction

Lignocellulosic biomass from land plants is the main cellulose source, the most abundant biopolymer, which comprises of a linear chain of connected glucose molecules. The term cellulose was coined by the French chemist Anselme Payen in 1838 (Credou & Berthelot, 2014). Since then, numerous in-depth studies have been conducted for easily obtaining this important material, producing minimal pollution in the process. Cellulose fibrils from plants comprise nanocrystals (3–20 nm in size) bound together through an amorphous phase, while lignin and some proteins function as a glue that holds fibrils together, thereby producing microfibers or bundles that are responsible for the great flexibility and endurance of higher plants (Mondal, 2017).

Recently, several xerophyte plants from the *agavoideae* subfamily have been studied as a source of cellulose for various applications (Pérez-Pimienta, López-Ortega, & Sanchez, 2017), mainly because of their low lignin content [9.8%], compared with other cellulose sources, and low cell wall recalcitrance (Li et al., 2014). Traditionally, the agave was used to produce fibers, food, and alcoholic beverages; however, recently it has been used to produce bioethanol (Li et al., 2014). Lately, research in the field of nanocellulose has been accelerating, particularly with studies on cellulose nanocrystals (CNC), bacterial cellulose (BC), cellulose nanofibers (CNF) (Faradilla et al., 2017; Trache, Hussin, Haafiz, & Thakur, 2017) and cellulose nanoplatelets (CNP) being published (Chávez-Guerrero et al., 2017). Several chemical approaches (e.g., concentrated acid, ionic liquids, enzymatic degradation, and TEMPO oxidation) and mechanical routes (e.g., high-pressure homogenizer, ultrasound, and milling) have been developed to extract nanocellulose from plants; however most of these approaches comprise several steps, that require intensive use of energy, reagents in high concentrations, and large amounts of water and solvents (Isogai, Saito, & Fukuzumi, 2011; Rahimi, Ulbrich, Coon, & Stahl, 2014; Xiang & Lee, 2000). Several studies have focused on improving the traditional methods of extracting cellulose (Chávez-Guerrero et al., 2017; Trache et al., 2017; Pérez-Pimienta et al., 2017) however, by changing the source of the raw material (biomass), these processes can also be optimized. Most of the approaches to obtain nanocellulose from agave use the same procedure as when wood it's used, without taking into account that agave has a lower recalcitrance, where several pretreatments like bleaching or mechanical milling and high sulfuric acid concentration [≈60%] during hydrolysis are applied to the raw material (Chávez-Guerrero et al., 2017; Pérez-Pimienta et al.,2017). Then, the

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development of easier alternative methods to extract cellulose remains a research goal of great importance, because nanocellulose its been used in flexible devices (Hoeng, Denneulin, & Bras, 2016), transparent films (Faradilla et al., 2017), solar cells and liquid fuels (Somerville, Youngs, Taylor, Davis, & Long, 2010) as well as a filler in polymers (Hoeng et al., 2016; Mondal, 2017). Agave shows considerable potential as a source of cellulose owing to its worldwide abundance, with a reported efficiency of up to 34 MT/ha/year of biomass (Somerville et al., 2010). This plant cultivated in semiarid lands is a low-cost feedstock. It is characterized by low recalcitrance and is an important source of glucose, galactose, sucrose, fructose and inulin (Li et al., 2012). Hence, we aim to describe the extraction conditions to obtain purified nanocellulose from agave powder (parenchyma) in one-pot and demonstrate the presence of platelet-like nanostructures comprising nanocellulose (CNP) through a facile chemical procedure that involves the use of small amount of reagents and leads to the isolation of other added-value chemicals (polysaccharides) besides cellulose.

2. Materials and methods

2.1. Materials

The sulfuric acid (95% w/w) and hydrogen peroxide (30% w/w), sodium hydroxide (pellets), 3,5 dinitrosalicylic acid, glucose powder, ethanol (anhydrous), deuterium oxide (99% D), were all of analytical grade and purchased from Sigma-Aldrich. Deionized water was used for all the experiments.

2.2. Cellulose extraction

Lignocellulosic raw material from *Agave salmiana* leave was washed with deionized water and freeze-dried for 48 h. Then, the lyophilized fragile agave samples (0.5 cm × 10 cm × 3 cm) were mechanically milled (Bel Art 37250 Micro-Mill Grinder) for 30 s to separate the agave into fiber (FA) and matrix (MA; Fig. S1). The MA was sieved (American standard #150) and subjected to the oxidation reaction in order to remove non-cellulosic materials. The sieved MA samples were treated with water (WA sample), hydrogen peroxide (PA sample) and low-concentration (0.17 M or 1.7 wt.%) sulfuric acid solution (SA sample), as shown in Fig. 1 (Table 1).

All dispersions were kept under stirring at 10 rpm for 10 min, then were placed inside an autoclave and kept isothermally at 120 °C under 1 kg/cm^2 vapor pressure for 45 min. All the dispersions were separated by centrifugation and washed with deionized water until a pH 6 was reached. A WA, PA and SA suspension was used to obtain the free-standing transparent films by solution casting method (Fig. S7). Then, the wet films were dried in an oven at 40 °C for 5 h.

Table 1
Amount of reagents for each sample.

CNPs Sample	Matrix	H_2O	H_2O_2	H_2SO_4
	(g)	(ml)	(ml)	(ml)
WA	1	200	0	0
PA	1	197	3	0
SA	1	195	3	2

2.3. Chemical and physical characterization of cellulose nanoplatelets

The chemical microstructure was further studied in a Thermo Scientific K-Alpha X-ray Photoelectron Spectrometer System. The analysis was done with monochromatized Al Kα radiation (E = 1486.68 eV). Survey and C1s high-resolution spectra were recorded for all cellulose samples using an energy pass of 50 eV. Cellulose films were fixed with double sided adhesive copper tape and placed in the analysis chamber at 10^{-9} mBar of vacuum pressure. The charging effect was corrected by shifting the binding energies considering the C1s signal at 285 eV. Nonlinear fit, using Gaussian curves was performed by maintaining the full-width at half-maximum (FWHM) constant for all components in a particularly high resolution spectrum.

Raman spectra measurements were recorded at room temperature using a Thermo Scientific DXR Raman microscope using a 532 nm laser excitation. Samples were deposited on a glass microscope slide and dried in an oven at 50 °C for 2 h. The spectral data were scanned for the acquisition of up to 30 accumulations and 30 s laser exposure time.

The morphology of samples was studied by SEM using a FEI NOVA NANOSEM 200. The samples were observed with an accelerating voltage of 10 kV and a working distance of 5 mm.

A drop of the sample dispersion (WA, PA and SA) and a drop of ethanol were deposited on a silicon wafer, and then it was dried at 40 °C for 2 h. Then, the silicon wafer was glued with graphite tape on top of an aluminum pin and coated with gold using a vacuum sputter coater.

A laser scanning microscope (LSM) was used to obtain height profiles with a ZEISS LSM 700, in order to study the topography of the sample using a laser emitting at 405 nm. Samples were glued with an adhesive carbon tape to a glass microscope slide. All images were acquired at 100 x magnification at 512 × 512 pixels, using at least 150 layers to build each image.

A Leica light microscope DM 3000 model was used to determine the

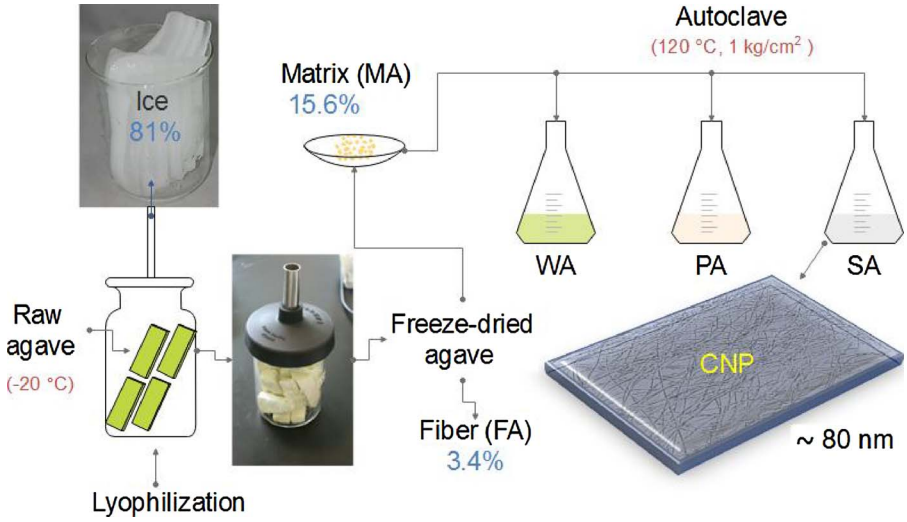

Fig. 1. Schematic procedure of the isolated cellulose nanoplatelets (CNPs). WA, water-treated sample; PA, hydrogen-treated sample; SA, dilute sulfuric acid solution-treated sample.