

Structural analysis and transformation of biosilica during lignocellulose fractionation of rice straw



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ABSTRACT

This study focused on the interfacial combination of silica and lignin-polysaccharides during lignocellulose fractionation of rice straw using scanning electric microscopy (SEM), x-ray photoelectron spectroscopy (XPS), and x-ray diffraction (XRD) techniques. Silica was deposited on the exterior surface of rice straw in the form of Si(OR)_x, Si–O–Si, SiO_x, and Si–C respectively, while not in the form of elemental Si. After delignification and alkalization, silica was deposited on the surface of polysaccharide with a more regular pattern. It is due to that silica reacted with polysaccharide to form SiO_x and Si(OR)_x during the decomposition of lignin and hemicellulose, leading to the remained framework structure of crystalline cellulose. After the decomposition of polysaccharide, silica was embedded into lignin fragments, and shown as an amorphous opal. For silica-lignin, Si–O–Si was gradually transferred to Si(OR)_x instead of Si–C. The capacities of the fractionated components to bind or store silica were in order of lignin > polysaccharides > lipids. Moreover, the fractionated components of rice straw were associated with the different ultrastructural forms of the silica.

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1. Introduction

Rice straw is renewable, widely, and available around the world [1]. In partially, there is around 200 million tons of rice straw annually produced in China [2]. As an abundant lignocellulosic biomass, rice straw has attracted interest as a potential source for profitable lignocellulose biorefinery, providing an alternative platform of the value-added chemicals and biofuels [3–5]. The utilization of rice straw as an alternative biomass can help protect environment.

Rice straw is composed of cellulose, hemicelluloses, lignin, and silica [6]. Cellulose is a linear biopolymer of anhydroglucopyranose, connected by β-1,4-glycosidic bonds. Hemicellulose, an amorphous branched heteropolymer of pentoses, hexoses, and sugar acid, is situated between lignin and a collection of cellulose underneath [1]. Lignin, a heteropolymer of phenolic subunits, acts as a protective shield giving strength to plant cells [7]. Silica, in general formula of [SiO_{n/2}(OH)_{4-n}]_m, acts as a protective shield from fungal diseases and ultraviolet radiation and provides the physical support

for rice yield [8–11]. Lignocellulose fractionation of rice straw would release the chemical components of cellulose, hemicellulose, lignin, and silica. These fractionated components can be further promoted new organic/inorganic chemicals, such as nanocrystalline cellulose, phenols, micro/nano silicon dioxide. Majority studies have shown that silica, polysaccharides and lignin could form a complex and rigid structure, leading to an inhibition during lignocellulose fractionation of rice straw [12–16]. However, it is not clearly that how the silica and lignin-polysaccharide are combined and how they affect the process of lignocellulose fractionation of rice straw.

Silica is a special property of rice straw, differing from other lignocellulosic biomass [17–19]. Rice is a typical silicon-accumulating plant, requiring large amounts of silicon for vigorous growth and high production. Silica is generally accumulated in cell walls of shoots, and in the intercellular region in the form of silica cell. Prychid et al. [20] studied the silicified structures in the *Poaceae*, and it can be subdivided into silica cells, dumbbell-shaped cells located on the vascular bundles, and silica bodies found on the bulliform cells of rice leaves. Zhang et al. [21] further pointed that silica cell in the leaf epidermis of *Oryza sativa*. L. develops gradually into dumbbell-shaped cells.

Silica is absorbed in the form of monosilicic acid, Si(OH)₄.

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Monosilicic acid follows water in the transpiration stream, and finally deposits as an amorphous opal (SiO_2). Fig. 1 illustrated the biosilicification of monomeric silicic acid to form larger silica particles proceeds [22,23]. It is also showed that cell wall of plant could be a matrix for self-assembly of silica. The organic environment within cell wall, including a vast range of proteins, lipids, metal ions, polysaccharides, and phenolic compounds, is likely to play an important role during the polymerization of silica.

Although the silica formation in the natural environment of silica bodies has been studies extensively, there is little information available on the transformation mechanism of silica during fractionation because the complex molecular structure of rice straw. Therefore, this study will examine the transformation of silica during lignocellulose fractionation process of rice straw. The combination between silica and lignin-polysaccharides are also investigated with scanning electric microscopy (SEM), x-ray photoelectron spectroscopy (XPS), and x-ray diffraction (XRD) techniques.

2. Material and methods

2.1. Materials

Rice straw was collected from a suburb near Nanjing City, China. The sample was hammered milled and the particles of 40–60 meshes were collected. Afterwards, rice straw was dried at 105 °C to a constant weight.

2.2. Lignocellulose fractionation of rice straw

The dried rice straw was firstly extracted with ethanol/toluene [2:1 (v/v)] for 6 h to obtain the lipids. After extraction, the lipids-free rice straw was treated with chlorite method at 70 °C for 2 h with stirrer to obtain the holocellulose. Subsequently, the holocellulose was hydrolyzed with 17.5 wt% alkali solution for the α -cellulose [24]. To determine the acid-insoluble (Klason) lignin, the lipids-free rice straw was hydrolyzed by 72 wt% H_2SO_4 and incubated at 18–20 °C for 3 h with stirrer. The sample was diluted with the distilled water to 3 wt% and boiled for 4 h. At last, the Klason lignin was filtered and washed [25]. The scheme of lignocellulose fractionation procedure of rice straw was presented in Fig. 2.

The total content of silica in the rice straw and in the fractionated components (lipids, holocellulose, α -cellulose, and Klason lignin) was measured according to the Chinese standard method [26]. The weighted sample was transferred to a crucible, carbonized gently over a burner, and then kept in a muffle furnace at 575 °C for 2 h. The resulted ash was immersed in the hydrochloric acid. The acid-insoluble residue was then filtered, and washed with the hot water until no chlorides were detectable, ignited, and finally weighted as silicon dioxide. All the tests were run repeatedly and the average percentage of SiO_2 in the rice straw and in the fractionated components was reported.

2.3. Surface morphology

A FEI company QUANTA 200 scanning electric microscopy (SEM) was used to observe the surface morphology of the fractionated components. The samples were coated with gold before examination.

2.4. XRD investigation

X-ray diffraction (XRD) was performed with an ultima IV diffractometer (Rigaku, Japan) with Cu K_α radiation ($\lambda = 0.15406$ nm), operating at 40 kV and 30 mA. The diffraction profile was detected using a locked couple 2θ scan from 5 to 50°. The samples were flatted into pellet form between two glass slides. The crystallinity index (*CrI*) of the samples was calculated according to Eq. (1):

$$CrI = \frac{I_{(002)} - I_{(am)}}{I_{(002)}} \times 100 \quad (1)$$

where, $I_{(002)}$ is the peak intensity at plane (200) in the XRD profile, and $I_{(am)}$ is the minimum intensity at the valley between plane (200) and (110) [27].

2.5. XPS analysis

X-ray photoelectron spectroscopy (XPS) was performed to determine the chemical composition of the fractionated components. A small quantity of sample was mounted on the double-sided adhesive tape and placed in a PHI5000 VersaProbe spectrometer (ULVAC-PHI, Japan) with a hemispherical energy analyser, using a monochromatic Al/K source (1486.6 eV). The XPS data were analyzed using the XPSPeak41 software, and the spectra of C1s, Si2p, and O1s in high-resolution were also obtained.

3. Results and discussions

3.1. Chemical components and SiO_2 yield

Table 1 showed the chemical components of rice straw and SiO_2 yield within the fractionated components. Rice straw was composed of polysaccharides, lignin, and lipids, and these components possessed the different capacities to bind or store silica. The lipids-free rice straw contained 11.10 wt% Klason lignin, and it possessed the total SiO_2 content of 34.46 wt% (90.5 mg/262.6 mg). The lipids-free rice straw contained 60.80 wt% holocellulose, which stored 7.51 wt% (106.6 mg/1419.9 mg) SiO_2 . Moreover, the lipids-free rice straw had 34.15 wt% of α -cellulose, containing 5.38 wt% (52.4 mg/974.5 mg) SiO_2 . Consequently, the capacities of the fractionated components to bind or store silica were in order of Klason lignin > polysaccharides > lipids.

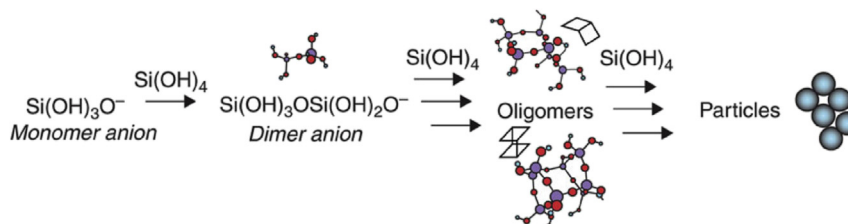


Fig. 1. The polymerization of monomeric silicic acid to form larger silica particles proceeds via biosilicification [22,23].

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