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# Synthesis of lignin-modified silica nanoparticles from black liquor of rice straw pulping

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ABSTRACT

A novel and green route was developed to prepare lignin-modified silica nanoparticles from black liquor by an integrated utilization strategy of rice straw. The lignin in black liquor was used as a structure directing reagent to control the particles' size, $CO_2$ obtained from the waste gas of pulp mills was used as a precipitating reagent and finally the lignin-modified silica nanoparticles were obtained. The effects of lignin concentration, pH and temperature on the properties of the materials have been investigated in detail, and the synthesis mechanism of the lignin-modified silica nanoparticles was proposed based on a series of experimental results.



## 1. Introduction

Silica nanoparticles have drawn much attention within the past decade due to their applications such as catalysts, humidity sensors, film substrates, electric and thermal insulators and fillers [1–3]. Up to now, many methods have been developed to synthesize silica nanostructures. For example, Pijiarn et al. [4] synthesized porous nanostructured pure silica having a high surface area from rice husk by sol-gel method. Cai et al. [5] prepared silica powders with an average size of 160 nm by pressured carbonation method. Jesionowski [6] described the preparation of spherical silica nanoparticles from an aqueous solution of sodium silicate and hydrochloric acid in cyclohexane medium via emulsion route. Panda et al. [7] reported the effects of varying gas-flow conditions on the characteristics of silica nanoparticles using diffusion flame technique. Of these methods, sol-gel method is widely applied due to low cost preparation and efficient size controlling. However, silica particles tend to agglomerate to large particles in wet colloids, which require additional material to prevent their agglomeration. Usually, surfactant [8–10] or emulsifier [6] was used to control particle size and avoid the agglomeration, but these materials are expensive and less environmentally friendly, and extensive use brings a lot of undesired scheduled waste. Moreover, materials used to prepared silica nanoparticles generally require complex processes and expensive organic precursors such as tetraethyl orthosilicate and cost-effective reagents like sodium silicate.

Black liquor of rice straw pulping contains organic materials (lignin, polysaccharides and resinous compounds of a low molar mass) and inorganic compounds (sodium hydroxide, sodium silicate and other soluble salt ions) in an aqueous medium [11]. Black liquor is traditionally burned in a recovery boiler to recover alkali chemicals and heat [12], but rice straw black liquor presents high silicon content. High silicon content inhibits the recovery of black liquor in alkali pulping processes [11,13], including the scaling formation in the evaporator, the reduction of heat transfer efficiency and the influence on causticizing treatment. Therefore, the waste recovery of silica is an effective strategy to avoid high silicon content in black liquor, and rice straw can be widely used in the future in regard to the shortage of traditional resources of fibrous raw material. Moreover, the waste industrial gas containing 20–40% $CO_2$ also brings environmental problems [14]. It is significant to convert industrial waste to a valuable product. Valuable chemical compounds contained in black liquor could be recovered, such as lignin [15]. However, the technological approach about the lignin-modified silica nanoparticles prepared from black liquor has not yet been reported.

In this paper, a novel and green route was developed to prepare lignin-modified silica nanoparticles with diameters ranging from 50 to 100 nm from black liquor by a sol-gel method. The in situ-modified $SiO_2$ nanostructures possess various advantages: (1) silicon in black liquor as industrial waste has been recovered by an integrated utilization strategy of rice straw, (2) lignin in black liquor has been used as a structure directing reagent to control the diameter of the silica nanoparticles and (3) $CO_2$ obtained from the waste gas of pulp mills has also been used as a precipitating reagent. The effects of lignin concentration, pH and temperature on the properties of the materials have been investigated in detail. The synthesis mechanism of the lignin-modified silica nanoparticles was proposed based on series of experimental results.

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## 2. Materials and methods

### 2.1. Materials

Black liquor of rice straw pulping was collected from ChenMing pulp mills in Jilin province China. Carbon dioxide ($CO_2$) and nitrogen ($N_2$) were from commercially pure gas in cylinders. Deionized water was applied for all synthesis and treatment processes.

### 2.2. Analysis of the composition of black liquor

The determination of silicon content of the black liquor was referred to Tong et al. [16], which is based on the silicon molybdenum blue photometric method. The lignin content of black liquor was measured according to Bu's method, which is based on an analysis for the typical absorption of 3.5-dinitrosalicylic acid in black liquor by the UV-visible spectrometry method [17].

### 2.3. Preparation of silica nanoparticles

The black liquor with a different lignin content was taken into a tube of which the ratio of length/diameter was 8. The tube was placed into a water bath at a given temperature. The mixture gas of $CO_2$ and $N_2$ was introduced into the bottom of the tube to simulate for the waste industrial gas. The flow rate of $CO_2$ and $N_2$ was 1.0 L/min and 0.4 L/min, respectively. The initial pH of black liquor was 11–12, and the final pH value of the black liquor was adjusted to the desired pH value accompanied by the mixture gas of $CO_2$ and $N_2$. $CO_2$ as a precipitating reagent lead to the formation of a silica colloidal in the solution. After aging for 1 h at the desired value of pH, the precipitate was collected by centrifugation. The precipitate was washed several times with water and then the final lignin-modified silica nanoparticles were obtained.

### 2.4. Characterization

The morphology and size of as-obtained samples were characterized on a Hitachi 4800 scanning electron microscope (FESEM) with an accelerating voltage of 15KV. The thermal behavior of the product was studied through thermal gravimetric analysis (TGA), which was performed with Melttler Toledo 825 instrument in air at a heating rate of 10 °C/min. Rourier transform infrared (FT-IR) spectroscopy experiment was performed on a SHIMADZU FT-IR 8400S spectrometer with the KBr pellet method.

## 3. Results and discussion

The silicon content and lignin content of rice straw black liquor was 0.4–1.1 wt% and 0.9–3.1 wt%, respectively. It is well known that a high silicon content faces problems, such as scaling in the recovery evaporator, reduction of the heat transfer efficiency and influence on causticizing treatment. It is necessary to remove silicon in order to reduce pollution and improve the efficiency of black liquor recovery in the alkali pulping processes. Experimental results show the silicon content of black liquor decreases to below 0.2% after the precipitation of silica nanoparticles.

To investigate the morphology evolution of the lignin-modified silica nanoparticles, the influence of the reaction parameters such as lignin concentration, pH value and reaction temperature were investigated, respectively. First, the effects of lignin concentration on the size of the particles are shown in Fig. 1. The experiments were performed with black liquor of different lignin content at 20 °C. The morphology of the particle is a typical spherical structure. Fig. 1a shows the SEM image of silica with lignin content of 1.1% in the system. The size of the particles did not appear to be uniform and large aggregations could be observed. Fig. 1 b-c illustrates the SEM images

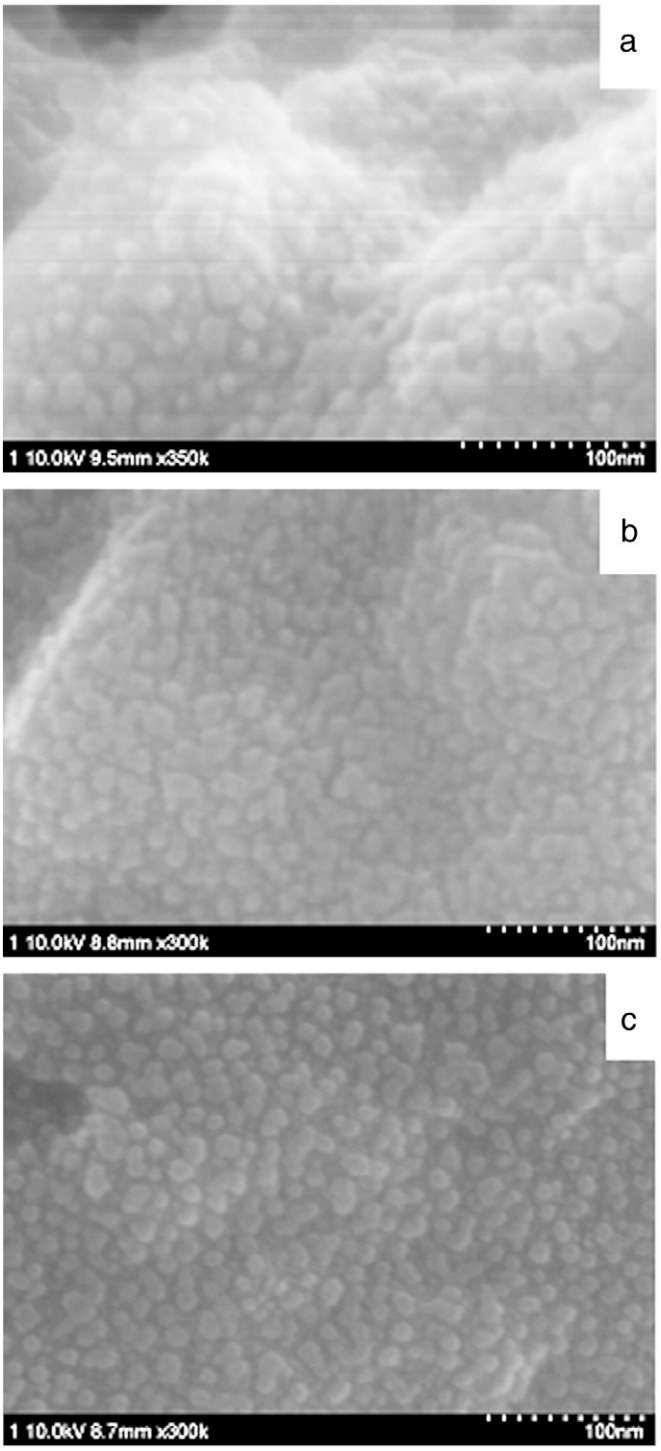


**Fig. 1.** SEM of lignin-modified silica nanoparticles prepared at pH 8.00 with different lignin content: (a) 1.1 wt%, (b) 1.8 wt% and (c) 2.7 wt%.

of the particles with lignin contents of 1.8% and 2.7%. It can clearly be seen that the size of the particles decreased. Silica particles with lignin content of 2.7% had diameters ranging from 50 to 100 nm and an average close to 80 nm without any large aggregation. No significant difference could be observed with percentages higher than 2.7% lignin in the system. This is due to the fact that in a wet silica colloid, the interface of silica and water contains the silanol group (Si-O-H) [18] which connects lignin molecules to form hydrogen bonds. The steric hindrance of lignin limits the aggregation of silica