



# A novel two-staged thermal synthesis method of generating nanosilica from rice husk via pre-pyrolysis combined with calcination



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## ABSTRACT

Rice husk is a promising precursor for producing amorphous nanosilica particles. Nanosilica particles with controllable surface areas and pore volumes have been obtained from rice husk using a novel two-staged thermal method via pre-pyrolysis combined with calcination. Nanosilica particles of different levels of purity and textural properties were produced under CO<sub>2</sub> and N<sub>2</sub> pyrolysis atmosphere within the temperature range of 300–800 °C. The materials synthesized at the designated pyrolysis temperature were characterized to have a purity of 95.85–99.62%, a specific surface area of 204.3–352.6 m<sup>2</sup>/g, and a total pore volume of 0.3513–0.5228 cm<sup>3</sup>/g. The morphology and non-crystal structure of the particles was studied by transmission electron microscope and X-ray powder diffractometer. The controllable textural characteristics allow these particles to be used in several scientific and technological fields, where different levels of purity and textural properties are required.

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## 1. Introduction

Silica is widely used in concrete, ceramic, rubber, composite filler, heat isolation, and photoelectric materials as well as in other fields. (Chandrasekhar et al., 2003; Kim et al., 2005). In particular, nanosilica with a large surface area (porous particles or particles of small size) has been increasingly applied in many hi-tech and fine manufacturing industries such as being used as photocatalysts, adsorbents, medicine, corrosion inhibitors, catalyst supports, and chromatography column packing materials (Adam et al., 2013; Awizar et al., 2013; Salavati-Niasari et al., 2013).

With the high content of natural silica, rice husk is a promising precursor material for producing amorphous nanosilica. Rice husk is an abundant agricultural residue in rice-producing countries. The estimated global rice production was approximately 678 million ton in 2009 (Alyosef et al., 2013), which resulted in approximately 140 million ton of rice husk. In addition, rice husk disposal becomes a great environmental threat to the land and the surrounding area in which it was dumped because rice husk is usually burnt in an open field or stacked on farmland, resulting in air pollution, energy waste, greenhouse gas emission, and occupancy of landfill space (Chen et al., 2011a; Johar et al., 2012). Therefore, the preparation of high-valued products from rice husk

is both economically beneficial and environmental friendly, such as the recovery of nanosilica from rice husk. The major constituents of rice husk are organic materials and hydrated silica; this silica is naturally amorphous and uniformly dispersed. Superfine silica powder of high purity can be prepared under controlled calcination conditions (Liou and Wu, 2010). For these reasons, the preparation technology of silica nanoparticles from rice husk is a very promising bio-resource technology.

Several researchers have reported different synthesis methods to prepare silica from rice husk, such as the sol-gel method (Le et al., 2013), chemical precipitation synthesis (Ma et al., 2011), and the calcination process (Ding and Su, 2012). The sol-gel method is based on the low-temperature hydrolysis and the condensation of molecular precursors (De Lima et al., 2011). The nanosilica obtained through this method is of high purity and homogeneity, but this synthesis route is time consuming (Zulkifli et al., 2013). Precipitated nanosilica is prepared by treating sodium silicate with inorganic acid in the course of precipitation. Although this method is simple, convenient and less consumable, the size of the obtained particles might be easily affected by some uncertain factors (Luo et al., 2012). In contrast, the calcination method is a more cost-effective means of nanosilica preparation from rice husk due to its simple process and stable performance.

After several decades of development, nanosilica particles obtained from the calcination process have been investigated in detail. The effects of pretreatment reagents (Ang et al., 2012; Chakraverty et al., 1988) and calcination parameters (Shen et al.,

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2011; Tzong-Horng, 2004) on the preparation of nanosilica from rice husk have been comprehensively explored as well as the kinetics of extraction and characterization of producing nanosilica particles from rice husk (Carmona et al., 2013). Umeda and Kondoh (2010) produced amorphous silica (99.5–99.77 wt%) from rice husk through polysaccharide hydrolysis and air combustion. Our research group prepared nanosilica particles with a silica content of 99.92% from rice husk using a pre-soaking method to improve the purity of the products (Gu et al., 2013). Previous work has mainly focused on the purity of the obtained silica and has attained high purity. However, some crucial parameters, such as the specific surface area and pore structure, of rice husk nanosilica were generally ignored. These parameters confer upon nanosilica particles special properties and applications, such as use as in medical, dental, cosmetic, or catalytic materials (Lazaro et al., 2013). Wang et al. (2011) synthesized semi-crystalline porous silica frameworks through the controlled melting catalyzed by  $K^+$ , but the silica was partly contaminated by the introduced  $K^+$  cations.

The aim of this research is to propose a novel two-staged thermal treatment method of nanosilica preparation from rice husk, in which pyrolysis was combined with calcination. In addition to a high purity, the pore structure and specific surface area of the products can be effectively controlled through the proposed method.  $CO_2$  and  $N_2$  were used as pyrolysis gases to change the internal structure of the rice husk and control the pore volume and specific surface area of the silica products. The whiteness, silica content, pore structure, and morphology of nanosilica were analyzed and discussed. This synthesis method allows for the production of nanosilica particles of controllable pore structure by tailoring the pyrolysis conditions. The controllable textural characteristics allow these particles to be used for different applications, where different levels of purity and textural properties are required.

## 2. Methods

### 2.1. Materials and reagents

Rice husk was collected from Lianyungang City in Jiangsu Province, China. The sample was soaked in deionized water at 20–25 °C, rinsed, dried at 110 °C, pulverized to approximately 60-mesh size, and then stored in a desiccator. The proximate analysis, ultimate analysis, and higher heating value are listed in Table 1. All of the chemical reagents, such as hydrochloric acid, were analytically pure and obtained from Beijing Chemicals Co., Ltd. (Beijing, China). All of the gases, such as purified nitrogen ( $N_2$ , 99.9995%), carbon dioxide ( $CO_2$ , 99.9%), and oxygen ( $O_2$ , 99.99%), were provided by Xinshiji Gases Co., Ltd. (Hangzhou, China).

**Table 1**  
Proximate analysis, ultimate analysis, and higher heating value of rice husk.

Characteristics	Rice husk
Proximate analysis <sup>a</sup>	
Moisture	2.03 wt%
Ash	13.18 wt%
Volatile matter	70.47 wt%
Fixed carbon	14.32 wt%
Ultimate analysis <sup>a</sup>	
Carbon	41.27 wt%
Hydrogen	5.12 wt%
Nitrogen	0.37 wt%
Sulfur	0.02 wt%
Oxygen	38.01 wt%
Heating value analysis <sup>b</sup>	3992 kcal/kg

<sup>a</sup> Dry basis.

<sup>b</sup> Higher heating value.

### 2.2. Preparation of nanosilica

Rice husk and hydrochloric acid (HCl, 8 wt%) were mixed into a 500 mL refluxing Erlenmeyer flask according the ratio of 1:10 (g:ml), heated to 120 °C, and the temperature was maintained for 4 h. The solid residue was rinsed to the neutral pH of 7 with distilled water and dried at 110 °C for 2–3 h for further processing. According to our previous work (Gu et al., 2013), the silica content of nanosilica increases with the increase of hydrolysis conditions. However, the use of a higher acid concentration and a higher hydrolysis temperature results in a decrease in the levels of purity of nanosilica and a higher ratio of RH to acid, and the hydrolysis time causes little increase in the levels of purity of nanosilica, but results in higher production cost.

$N_2$  and  $CO_2$  were utilized in the different experiments as pyrolysis gases.  $O_2$  was utilized in the experiments as an oxidation gas. A mass flow controller was used to control the flow rate of the gases. A tubular furnace was used to supply the heat for the pyrolysis and oxidation reactions. In the beginning of each test, 5 g of acid-leached rice husk was placed into a semi-column crucible in the furnace at room temperature; the furnace was pre-evacuated to guarantee a subsequent pyrolysis atmosphere. Next, pyrolysis gas was constantly pumped into the furnace at a flow rate of 1 L/min. The furnace was heated to the designated pyrolysis temperature (300–800 °C) at a constant heating rate of 20 K/min, and then, the temperature was maintained for 30 min. Subsequently,  $O_2$  was supplied into the furnace instead of the pyrolysis gas with a flow rate of 1 L/min. The pyrolyzed rice husk was calcined under a heating rate of 10 K/min at 610 °C for 2–3 h to remove organic compounds to form nanosilica powder. The determination of the calcination temperature was described in our previous work (Gu et al., 2013). That is, the pyrolyzation of rice husk at high temperatures reduces the carbon content and enhances the levels of purity of nanosilica, but excessively high temperatures inhibit the destruction of Si–C bonding, resulting in a higher carbon content that decreases the silica content of nanosilica. All of the measurements were repeated three times to reduce errors.

### 2.3. Analysis

The silica content of the samples was measured according to the Standard Test Method ASTM E 247-1996. The whiteness of the samples was measured by using a colorimeter (WSB-III, Shanghai, China).

The specific surface area was evaluated by using the Brunauer–Emmett–Teller (BET) model in the relative pressure range ( $P/P_0$ ) between 0.05 and 0.25, where  $P$  is the system pressure, and  $P_0$  is the initial pressure (1 bar in this experiment). The pore volume of silica nanoparticles was determined by the nitrogen adsorption isotherm at a relative pressure  $P/P_0$  of 0.3 using a pore size analyzer Omnisorp 100CX (Beckman Coulter, USA).

The non-crystal state of the nanosilica particles was analyzed by an X'Pert PRO powder diffractometer equipped with a Ni-filtered Cu-K $\alpha$  ( $\lambda = 1.54059 \text{ \AA}$ ) radiation source driven at 40 kV and 45 mA, with diffraction patterns collected over the  $2\theta$  scan range from 5° to 60°.

The morphologies and particle sizes of the samples were investigated using a transmission electron microscope (Tecnai G2 F30 S-Twin TEM, NL). The samples were ultrasonically dispersed in ethanol for 15 min before imaging.

## 3. Results and discussion

### 3.1. Silica content and whiteness analysis

The silica content and whiteness of nanosilica particles prepared under  $CO_2/O_2$  and  $N_2/O_2$  atmospheres at different pyrolysis

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