Facile Synthesis of Mesoporous Silica Aerogels from Rice Straw Ash-based Biosilica *via* Freeze-drying

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The combustion of biomass fuels has been a significant source of global energy, and about 10 million tons of straw are used annually, yielding at least 0.5 million tons of straw ash. However, the ash from rice straw has rarely been reused, thereby contributing to environmental pollution. A new approach is reported for preparing mesoporous silica aerogels using straw ash-based biosilica *via* a sol-gel process and vacuum freezedrying. The mesoporous structure, porosity, pore volume, and specific surface area of this straw ash-based aerogel had satisfactory values. Effects of pH on the synthesis of silica aerogel were investigated to better understand the most important factors influencing the gelation, final structure, physicochemical properties, morphology, and thermostability of the samples.

Keywords: Silica aerogel; Rice Straw ash; Biosilica; Freeze-drying; BET

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INTRODUCTION

Silica aerogel (SA) is a highly porous nanostructured material that exhibits extraordinary properties, such as a large surface area, high porosity, low density, low thermal conductivity, and low index of refraction (Hegde and Rao 2006; Cui *et al.* 2011; Wang *et al.* 2016; Yu *et al.* 2016). Silica aerogels can be prepared from various silicon materials (Kanamori *et al.* 2007; Aghajamali *et al.* 2016; Wang *et al.* 2017b) and are synthesized *via* sol-gel processes and different drying methods such as supercritical drying (Yu *et al.* 2016) and ambient pressure drying (Yun *et al.* 2017).

Some natural bioresources contain a large amount of silicon. The role of silicon in natural bioresources has been overlooked for a long time (Jin *et al.* 2014). In most bioresource species, particularly those belonging to the Gramineae family, aqueous silicic acid $(Si(OH)_4)$ is transported along the transpiration stream in the plant, where polymerization occurs as a result of an increase in the silicic acid concentration. At the end of polymerization, silicon is deposited into the cells and intercellular spaces (Chen *et al.* 2010). Rice plants accumulate silica *via* the polymerization of water-soluble silicic acid (H₄SiO₄), which is absorbed from the soil, into insoluble polysilicic acids. This is followed by precipitation, in the form of amorphous silica, which is deposited on the exterior cell walls of a plant (Van Soest 2006). In this process, the rice acts as a biorefinery factory for high-quality amorphous silica.

In recent years, approximately 12% of the global energy is generated by the combustion of biomass fuels, and around 35% of the energy comes from biomass in developing countries. About 30 to 40% of the biomass comes from straw. More than 0.7 billion tons of straw are produced annually in China, wherein approximately 10 million

tons of straw are used for generating electricity by means of combustion, which produces at least 0.5 million tons of straw ash (Cai *et al.* 2013). Meanwhile, the global annual rice residue output is estimated to be approximately 600 million tons, and the rice straw ash produces more quantitative silica than other biomass ash (Abdel-Mohdy *et al.* 2009). However, the lack of recycling technology makes rice straw ash hard to reuse, bringing about a large contribution to environmental pollution (Bageru and Srivastava 2018). Therefore, it is necessary to develop an effective technology for the utilization of rice straw ash. The utilization of Si resource from rice husk has been reported (Banerjee *et al.* 1982; Conradt *et al.* 1992; Liou and Wu 2010; Lu and Hsieh 2012; Yang *et al.* 2018b) but the use of silicon from rice straw ash has been rarely considered.

According to a recent study, the authors showed that rice straw ash produced more than 80% of silicon, achieving a high yield at a low cost (Yang *et al.* 2018b). Herein, this work prepared mesoporous SAs from silicon that had been extracted from RS *via* combustion (the product is RS ash) and an alkali treatment to remove impurity. Then the SA was synthesized from RS ash-based silicon *via* a sol-gel process and vacuum freeze-drying, which was a new approach. Supercritical drying and ambient pressure drying are commonly used technologies, but they have their limitations. For instance, supercritical drying equipment is complex, and the processing cost is very high, while ambient pressure drying method is hardly able to obtain stable structure of SA, making it necessary to use additives to consolidate the skeleton of SA (Wang *et al.* 2017a; Zhao *et al.* 2017).

The RS ash-based SA from this work had a low density, high porosity, strong adsorbability, large surface area, and good thermal properties. The effects of the pH on the synthesis of SA were investigated to better understand the most important factors that influence the gelation, final structure, physicochemical properties, morphology, and thermostability of the samples. This novel method employs natural, environmentally friendly bioresources and avoided the use of complicated supercritical CO_2 drying technology.

EXPERIMENTAL

Materials

Rice straw (40 mesh to 60 mesh size) was collected from a farm in Nanjing (Jiangsu province, China). Sodium hydroxide (Sigma-Aldrich, Shanghai, China), concentrated sulfuric acid (98% in purity) (Sigma-Aldrich, Shanghai, China), and ethyl alcohol (99.5% in purity) (Sigma-Aldrich, Shanghai, China) were also used in this study.

Methods

Rice straw-based sodium silicate preparation

The RS was washed with deionized water to remove soil and other contaminants. Then, the RS was burned inside of a muffle furnace (Siom, Shanghai, China) at 600 °C for 4 h to obtain RS ash. Twenty grams of RS ash were dispersed into 100 mL of 5% (v/v) NaOH aqueous solution and heated at 100 °C for 2.5 h under vigorous stirring to dissolve the silica and produce sodium silicate (Fig. 1). The purity of silica was above 80% according to XPFS analysis (ThermoFisher, Shanghai, China).

Silica aerogel synthesis

The RS-based sodium silicate was allowed to cool to room temperature, and H₂SO₄ was added to four samples of the solution to adjust the pH to 6, 7, 8, and 9. After vigorous stirring for 4 h, the samples were set aside for another 24 h to allow the silica gel to slowly precipitate (Lu and Hsieh 2012). Then, the samples were washed with deionized water to remove the sodium, and the hydrogels were obtained. The RS-based hydrogels were solvent-exchanged with ethyl alcohol for 72 h to replace the water. The ethyl alcohol solution was changed every 24 h. The RS-based alcogels were then formed. The alcogel samples were quickly frozen in a refrigerator at -20 °C and freeze-dried in a vacuum freeze-dryer (LGJ-18A, Bilon, Shanghai, China) for 24 h at -30 °C to remove the ethyl alcohol. The freeze-dried products were dried in a vacuum desiccator at 20 °C for 24 h to obtain four RS-based SA samples with different pH values (Fig. 1), which were labeled as A-6, A-7, A-8, and A-9.

Conventional characterization

The bulk density of the obtained RS-based aerogels was calculated from the mass to volume ratio of the gel (Zhang *et al.* 2016). The porosity was determined from the ratio of the measured bulk density to the theoretical density ($\rho_s = \sim 2.2 \text{g/cm}^3$) using Eq. 1 (Li *et al.* 2016):

Porosity (%) =
$$(1 - \rho_b / \rho_s) \times 100\%$$
 (1)

where ρ_b is the bulk density (g/cm³) and ρ_s is the theoretical density (g/cm³).

The volume shrinkage percentage (V_s) was determined with Eq. 2 (Rao *et al.* 2006):

$$V_{\rm s}\,(\%) = (1 - V_{\rm a} \,/\, V_{\rm g}) \times 100\% \tag{2}$$

where V_a and V_g are the volumes (g) of the straw-based aerogel and alcogel, respectively.

N₂ sorption isotherms

The specific surface area (*A*) and pore volume (V_{pore}) were measured *via* the multipoint Brunauer–Emmett–Teller (BET) method with an ASAP 2020 analyzer (Micromeritics Instrument Corp., Norcross, GA, USA), based on nitrogen adsorption–desorption isotherms (Wang *et al.* 2017a). Before the measurement, the samples were degassed at 120 °C for 24 h until the mass reached a constant value. The pore size distribution was evaluated using the Barrett–Joyner–Halenda (BJH) method (Yu *et al.* 2016).

Micromorphological features

The microstructure and surface morphology of the samples were examined *via* field emission scanning electron microscopy (FE-SEM) (S4800, HITACHI, Tokyo, Japan). The samples were attached to an aluminum specimen mount with conductive carbon tape (Yang *et al.* 2018a) and sputter coated with gold under vacuum at 20 mA for 20 min. The samples were observed and imaged at an accelerating voltage of 5 kV.

Thermogravimetric and differential scanning calorimetry analysis

The thermogravimetric (TG) and differential scanning calorimetry (DSC) analyses of the SAs were performed using TG 209 F3 (NETZSCH, Selb, Bavaria, Germany) and DSC 200 F3 thermal analyzers (NETZSCH, Selb, Bavaria, Germany),

respectively. For the TG test, the SA samples were heated from room temperature to 900 °C in an air atmosphere (80% N₂ and 20% O₂) (Li *et al.* 2016) at a heating rate of 10 °C/min. For the DSC test, the SA samples were heated from room temperature to 600 °C at a heating rate of 10 °C/min. The weight change and heat flux, with respect to the temperature, were recorded with the Proteus software (NETZSCH, Selb, Germany). Each heating rate was tested in triplicate, and the experimental results showed excellent repeatability.

RESULTS AND DISCUSSION

Synthesis of the Rice Straw-based Silica Aerogels

Silica aerogels are generally synthesized by hydrolyzing and condensing water glasses or silicon alkoxides to form gels. It has been reported that the gelation time is greatly influenced by the solution pH (Yun et al. 2017). In the present study, no gel formation was observed in a solution with a pH of 6. Gel formation occurred when the pH was greater than or equal to 7. The gelation time sharply decreased as the pH increased, and less time was required for gel formation when the pH was 8. It was noteworthy that a precipitate was observed at a pH of 9 because of rapid hydrolysis. Figure 1 presents the synthesis process of the RS-based SAs from hydrogels to aerogels at different pH values. Figures 2a, 2b, and 2c show the RS-based hydrogels produced from the RS materials. The morphological features of the hydrogels were similar under different pH conditions; the samples were translucent and jelly-like. The alcogel samples that were exchanged with ethyl alcohol for 24 h to replace the water are shown in Figs. 2d, 2e, and 2f. There was a delicate feature seen in the alcogel in Fig. 2f, in which flocculants formed because of the higher pH value. Figures 2g, 2h, and 2i show that the alcogels that had been exchanged for 72 h had different morphologies at different pH values. The alcogel sample with a pH of 7 shrunk (Fig. 2g), while the alcogel sample with a pH of 8 (Fig. 2h) was turbid and contained flocculent materials. Precipitates were observed in the alcogel sample with a pH of 9 (Fig. 2i). Moreover, the morphologies of the RS-based aerogels were also different (Figs. 2j, 2k, and 2l). Sample A-7 was a semilucent white, unbroken aerogel that could be removed from the container by hand and could keep its shape well (Fig. 2j). The A-8 sample exhibited multiple fragments around a larger piece, and only the large part could be removed (Fig. 2k). Sample A-8 had a darker color, *i.e.*, milk white, and was not as homogeneous as A-7. At a pH of 9, it was hard to form an integrated aerogel and numerous fragments can be seen in the container (Fig. 21).

The bulk density, porosity, volume shrinkage, specific surface area, pore volume, and average pore size of the RS-based aerogels prepared at different pH values are listed in Table 1. The gelation of silica sol is greatly influenced by the pH of the solution. Therefore, no gels were formed at a pH of 6, and a precipitate was observed at a pH of 9. The physical properties of the RS-based aerogels were shown to meet the standards for SAs.

Table	1. Effects	of the pH	on the	Physical	and T	Textural	Properties	of the I	RS-
based	SAs								

Sample	pH Value	Bulk Density (g/cm ³)	Porosity (%)	Vs (%)	S _{BET} (m²/g)	V _{Pore} (cm³/g)	Average Pore Size (nm)
A-6	6	No gel in 72 h	-	-	-	-	-
A-7	7	0.22	91.18	23.60	332.73	1.80	15
A-8	8	0.19	90.01	17.80	154.30	0.33	8
A-9	9	Precipitate	-	-	-	-	-

SBET - BET surface area



Fig. 1. Photographs of the preparation steps of the RS-based SAs from hydrogels to aerogels: RS-based hydrogels at a pH of (a) 7, (b) 8, and (c) 9; RS-based hydrogels alcohol-exchanged for 24 h at a pH of (d) 7, (e) 8, and (f) 9; RS-based alcogels alcohol-exchanged for 72 h at a pH of (g) 7, (h) 8, and (I) 9; and RS-based aerogels at a pH of (j) 7, (k) 8, and (I) 9

The A-7 and A-8 porosities were above 90%, and the bulk density was approximately 0.2 g/cm³, which indicated that the RS-based SA samples displayed typical characteristics for mesoporous materials with a high porosity. Moreover, the specific surface area was high. The physical properties of the SAs were also obviously affected by the pH.



Fig. 2. Analysis of the nitrogen adsorption-desorption isotherms and pore size distributions: (a) N_2 sorption isotherms of the SiO₂ aerogels at 350 °C and (b) pore size distributions of the SiO₂ aerogels

The A-7 sample showed the highest porosity (91.2%) and specific surface area $(332.7 \text{ m}^2/\text{g})$, as well as the lowest volume shrinkage (23.6%) and bulk density (0.22 g/cm^3) , which are positive characteristics for porous materials. This may have been because of network strengthening at this pH value, which resulted in less dimensional shrinkage of the silica skeleton and less collapse of the pores (Yu *et al.* 2016). This

behavior was also evident from the average pore volume $(1.80 \text{ cm}^3/\text{g})$ and pore size (15 nm) of A-7. An appropriate pH value can form remarkably larger silica particles with bigger pore sizes, as was revealed by the SEM images. The A-8 sample had a smaller porosity (90.01%) and a bulk density of 0.19 g/cm³. The average pore size was 8 nm and the pore volume was 0.33 cm³/g; therefore, A-8 had a great mesoporous structure.

The nitrogen adsorption-desorption isotherms of the RS-based SAs are presented in Fig. 3a, and the corresponding BJH pore size distributions are shown in Fig. 3b. The isotherms of A-7 and A-8 were type IV, meaning that they exhibited hysteresis between the adsorption and desorption branches, per the International Union of Pure and Applied Chemistry (IUPAC) classification, which indicated the mass existence of mesopores in the prepared aerogels.

The rounded knee at low pressures indicated the approximate location of a monolayer formed by minor micropores. The nitrogen adsorption rate increased quickly in the middle-pressure range, but it increased slowly in the high-pressure area (Fig. 3a). The gentle slope in the middle of the isotherms indicated multilayer adsorption of nitrogen on the surface, as well as type II hysteresis (IUPAC classification).

The pore-size distribution (Fig. 3b) was consistent with nitrogen physisorption isotherms. There was a peak between 5 nm and 18 nm for the A-7 aerogel and between 5 nm and 18 nm for the A-8 aerogel, which indicated that the former had a higher specific surface area and adsorption capacity.

Scanning Electron Microscopy Analysis

The SEM analysis revealed the microstructures of the straw-based aerogels, as can be seen in Fig. 4. The samples treated at different pH values displayed typical features of mesoporous materials. The A-7 sphere had a classical three-dimensional network (Yu *et al.* 2016) that consisted of interconnected particles (Fig. 4a). Moreover, the pores of A-7 were bigger than those of A-8 (Fig. 4b), which was consistent with the pore size distribution evaluation using the BJH method (Fig. 3).

The aerogel that formed at a pH of 7 may have had an increased solvent exchange rate. Wet gels are more conducive to extraction during the drying process. The network structure of A-8 (Fig. 4b) was different from that of A-7, with smaller pore sizes, which agreed with the BET analysis in Fig. 3b. However, the A-8 sample, with a smaller surface area and slightly worse dimensional network, was easier to crush and exhibited a lower adsorbability (Fig. 4b).

The high magnification images show that A-7 possessed a more visible aerogel skeleton and well distributed pores (Fig. 4c) compared with that of A-8, which indicated that the pH value of the solution had a major effect on the morphology. Moreover, the pore size of A-8 was smaller than that of A-7, which coincided with the absorption curve (Fig. 4d).

In general, the porous skeleton easily collapsed when using other drying methods except for supercritical drying because of the dimensional shrinkage. But the appropriate pH value in this work and low temperature from the freeze drying method inhibit the active particles from agglomeration, which formed the stable mesoporous skeleton structure. Therefore, the pore dimensional network had better structure than reported in previous research.



Fig. 3. SEM images of the RS-based aerogels prepared at a pH of (a) 7 and (b) 8; High magnification images of the samples prepared at a pH of (c) 7 and (d) 8

Thermogravimetric and Differential Scanning Calorimetry Analyses

The TG analysis was conducted to investigate the thermal decomposition properties of the RS-based aerogels.

Figure 5 shows that the TG and DTG analyses of the RS-based aerogels were performed in air between 35 °C and 600 °C. The total weight losses of the A-7 and A-8 aerogels were 14.05% and 18.63%, respectively. The weight loss from 30 °C to 150 °C corresponded to the adsorption of water and residual solvents.

In the range of 150 °C to 600 °C, the mass loss was lower, especially at a pH of 7. The A-8 aerogel possessed a higher weight loss ratio, which could have been because of the easy degradation of alkaline SAs *via* oxidation. This implied A-8 had a higher thermal stability than the A-7 aerogel.



Fig. 4. TG and DTG curves of the RS-based aerogels

CONCLUSIONS

- 1. It was demonstrated that high-quality mesoporous SAs could be prepared using sodium silicate extracted from rice straw ash-based biosilica, and the rice straw ash-based SAs had better characteristic.
- 2. Different pH values were used to comparatively study the effects of the pH on gelation. It was demonstrated that the pH is one of the most important factors that influences the preparation of RS ash-based SAs.

- 3. The microstructural ordering of mesoporous silica depended on the pH, and a pH of 7 led to a well ordered and typical three-dimensional porous structure. Additionally, the mesoporous structure, porosity, pore volume, and specific surface area of this RS-based aerogel had satisfactory values.
- 4. Without any need to employ additives, one can obtain excellent pore network structure when using freeze drying to fabricate the rice straw ash-based SAs, while replacing the complicated supercritical drying.

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