

## Preparation of Nano Size Silica from Rice Hull Ash

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The effect of different concentrations of sodium silicate solution and adding speeds of H<sub>2</sub>SO<sub>4</sub> solution (10 %, w/w) on the size of nano-silica were investigated. The optimum preparation method of small size nano-silica involved the mixing of sodium silicate solution (11.8 %) and the adding speed of H<sub>2</sub>SO<sub>4</sub> solution (14.5 mL/min) and its size was 30 nm. The fourier transform infrared suggested that the product contained all characteristic peaks and groups of silica. The result from X-ray diffraction pattern suggested that the amorphous characteristic peak of the product occurred at  $2\theta = 22.5^\circ$ . Transmission electron microscopy image revealed that the size was about 30 nm and the product was a little agglomerative.

**Key Words:** Preparation, Nano-silica, Rice hull ash.

### INTRODUCTION

Silica can increase the strength and resisting-friction of plastics, the strength of white paper, improve the effect of coatings, the fluidity and resisting-electron of drugs and keep the fruit and vegetable fresh<sup>1-3</sup>. Especially, silica can greatly increase the strength of rubber<sup>4</sup>. The size is the most important characteristic of the silica. The smaller the size of silica is, the better performance<sup>5</sup>. Rice hull ash (RHA) contained silicon (ca. 20 %) <sup>6</sup>. Many researchers recently focused on preparation of silica from RHA. In previous works, Li and Wang<sup>7</sup> investigated preparation of silica aerogel from RHA by drying at atmospheric pressure. Tang and Wang<sup>8</sup> investigated the preparation of silica aerogel from RHA by supercritical carbon dioxide drying. Silica aerogel could not be widely used in industry because it was too costly<sup>7,8</sup>. Kalapathy *et al.*<sup>9</sup>, investigated preparation of pure silica by washing RHA and dried silica gel. Kalapathy *et al.*<sup>10</sup> investigated preparation of silica at pH 4.0 by adding silicate solution to acidic solution.

Concentration of sodium silicate solution and adding speed of acid solution are the most important factors affecting the size of nano-silica<sup>9,10</sup>. However, there were no reports on preparation of small size nano-silica by controlling concentration of sodium silicate solution and adding speed of acid. The objective of this study is to prepare small size nano-silica from RHA by controlling concentration of sodium silicate solution and adding speed of acid solution. Small size nano-

silica was characterized by fourier transform infrared (FT-IR), X-ray diffraction (XRD) and transmission electron microscopy (TEM) image.

### EXPERIMENTAL

Rice hull ash was purchased from rice processing company of Jiangxi in China. All other chemicals and reagents were of analytical grade unless otherwise noted.

**Preparation of sodium silicate solution:** Rice hull ash (150 g) and NaOH solution (1.5 mol/L, 1000 mL) were added in a 2000 mL flask and mixed. The mixture was boiled at 100 °C for 2 h with stirring at 250 rpm and condensation. The boiled solution was filtered through Whatman No. 41 ashless filter paper and the filter cake was washed using 1000 mL of boiling water<sup>9,10</sup>. The filtrate was sodium silicate solution.

**Measurement of concentration of sodium silicate solution:** The measurement method of concentration of sodium silicate solution was as follows (referred to the Standard GB/T 4209-2008 of China). Sodium silicate solution (5.0000 g) was diluted using water in a 250 mL volumetric flask. 50 mL of the diluted solution was added in a 300 mL conical flask. The diluted sodium silicate solution was titrated using 0.5 mol/l HCl standard titration solution until the solution turned into red. Then the diluted sodium silicate solution was titrated using 0.5 mol/L NaOH standard titration solution until the solution turned from red into yellow. The volumes of HCl and NaOH solution consumed were recorded. Meanwhile a contrasted

experiment was carried out. The concentration of sodium silicate solution (C) was calculated according to the equation:

$$C = \frac{[(c_1 \times V_1 - c_2 \times V_2) - (c_1 \times V_3 - c_2 \times V_4)] \times 0.01502}{m \times \frac{50}{250}} \times 100$$

$$= \frac{[(c_1 \times V_1 - c_2 \times V_2) - (c_1 \times V_3 - c_2 \times V_4)] \times 7.510}{m}$$

in the equation:  $c_1$  = concentration of HCl standard titration solution (mol/L);  $c_2$  = concentration of NaOH standard titration solution (mol/L);  $V_1$  = volume of HCl standard titration solution consumed (mL);  $V_2$  = volume of NaOH standard titration solution consumed (mL);  $V_3$  = volume of HCl standard titration solution consumed in the contrasted experiment (mL);  $V_4$  = volume of NaOH standard titration solution consumed in the contrasted experiment (mL);  $m$  = mass of sodium silicate solution (g); 0.01502 = mass of  $\text{SiO}_2$  (g) equivalent to 1.00 mL of HCl standard titration solution (1.000 mol/L).

Different concentrations of sodium silicate solution were obtained through concentrating.

### Selection of preparation method of small size nano-silica

**Orthogonal experiment design:** Concentration of sodium silicate solution and adding speed of  $\text{H}_2\text{SO}_4$  solution (10 %, w/w) were used as the controllable factors. Their levels were listed in Table-1. An orthogonal array  $L_4(2^3)$  was used to determine the optimum preparation method of small size nano-silica (Table-2).

TABLE-1  
FACTORS AND LEVELS DESIGN OF  
THE ORTHOGONAL EXPERIMENT

Level	Concentration of sodium silicate solution (%) (A)	Adding speed of $\text{H}_2\text{SO}_4$ solution (B)
1	9.8	10.5
2	11.8	14.5
3	13.8	18.5

TABLE-2  
ORTHOGONAL ARRAY\*

Sample	A	B	Size (nm)
L1	1	1	$70 \pm 4^a$
L2	1	2	$50 \pm 4^b$
L3	1	3	$80 \pm 4^c$
L4	2	1	$60 \pm 4^d$
L5	2	2	$30 \pm 4^e$
L6	2	3	$50 \pm 4^f$
L7	3	1	$70 \pm 4^g$
L8	3	2	$60 \pm 4^h$
L9	3	3	$110 \pm 4^i$
$K_1$ (nm)	170	170	–
$K_2$ (nm)	110	100	–
$K_3$ (nm)	190	210	–
Variance (nm)	80	110	–

\*Values are means  $\pm$  SD ( $n = 3$ ). Values followed by the different letter in the same column are significantly different ( $p \leq 0.05$ ).

**Preparation of different size nano-silica samples:** Different concentrations of sodium silicate solutions (300 mL) were added in a 500 mL flask and heated at 80 °C in water bath with stirring at 250 rpm and condensation<sup>9,10</sup>. Sulfuric acid (10 %, w/w) solution was then added dropwise to the flask at different speeds by a constant flow pump<sup>9,10</sup>. Sulfuric acid

solution (10 %, w/w) was stopped adding until the pH of the gels were kept at a same level (*ca.* 9.7)<sup>9,10</sup>. These gels were incubated at 80 °C for 90 min and treated by an Ultrasonic Cell Muller at 90 w for 15 min<sup>11</sup>. Then they were centrifuged at 3000 rpm for 10 min and filtered through Whatman ashless filter paper<sup>12</sup>. The filtered cakes were repeatedly washed using deionized water until no  $\text{SO}_4^{2-}$  left by checking with  $\text{BaCl}_2$  solution<sup>11</sup>. The filtered cakes were dried at 80 °C for 12 h to get different sizes of nano-silica samples.

**Measuring the size of nano-silica samples:** Nano-silica sample (1 g) was grinded for 1 min on a Jiuyang Muller. The powder was made to 0.005 % anhydrous alcohol solution. The solution was treated by Ultrasonic Cell Muller at 90 w for 10 min. It was used to measure the size of nano-silica by a nano-zs size/zeta potential apparatus with 163.8 kcps count rate and 10 attenuating frequency. The optimum preparation method was selected according to the smaller size.

**Characterization of small size nano-silica:** Small size nano-silica was characterized by FT-IR, XRD and TEM image. Their test conditions were listed in Table-3<sup>12</sup>.

TABLE-3  
TEST CONDITIONS OF FT-IR, XRD AND TEM IMAGE

Characterization method	Test equipment	Test conditions
FT-IR	Nicolet Nexus 470 FT-IR spectrometer (Thermo Electron Company, America)	Scanning rate: 32 times/min; resolution: 4 $\text{cm}^{-1}$
XRD	D8 Advance Bruker Rotaflex Diffractometer (Bruker Axs Company, German)	Acceleration voltage: 40 kV; current: 45 mA; 2 $\theta$ : from 10-40°; rate: 5°/min
TEM image	JEM-2010 microscopy (Jeol, Japan)	Voltage: 200 kV; current: 80 mA

**Statistical analysis:** Statistical analysis was carried out using Origin 7.5 (Origin Lab. Inc., USA).

## RESULTS AND DISCUSSION

**Determination of preparation method of small size nano-silica:** The size data of different nano-silica samples were listed in Table-2. Among these samples, the size was the smallest (30 nm) when the concentration of sodium silicate solution was 11.8 % and the adding speed of  $\text{H}_2\text{SO}_4$  solution (10 %, w/w) was 14.5 mL/min. Nano-silica gel particle increased and agglomerated fast when the concentration of sodium silicate solution was too high or low and the adding speed of  $\text{H}_2\text{SO}_4$  solution (10 %, w/w) was too quick or slow. According to the variance, the effect of adding speed of  $\text{H}_2\text{SO}_4$  solution (10 %, w/w) on size was greater than the concentration of sodium silicate solution because increasing and agglomeration of nano-silica gel particle was mainly depend on  $[\text{H}^+]$ .

### Characterization of small size nano-silica

**FT-IR pattern analysis:** FT-IR pattern of small size nano-silica was shown in Fig. 1. The peak near 3420  $\text{cm}^{-1}$  was the stretching vibration characteristic peak of -OH group. The peak near 1626  $\text{cm}^{-1}$  was the bending vibration characteristic peak of -OH group. The two peaks were mainly caused by physically absorbed water and crystal water<sup>11,13</sup>. The peak near 1103  $\text{cm}^{-1}$

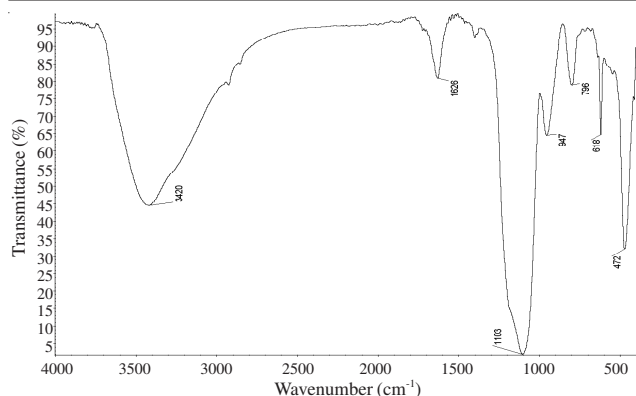


Fig. 1. FT-IR pattern of small size nano-silica

was the symmetric stretching vibration characteristic peak of Si-O-Si group<sup>11,13</sup>. The peak near 947 cm<sup>-1</sup> was due to the asymmetric stretching vibration characteristic peak of Si-O-Si group<sup>11,13</sup>. The peak near 472 cm<sup>-1</sup> was the bending vibration characteristic peak of Si-O-Si group<sup>11,13</sup>. The peak near 796 cm<sup>-1</sup> was the stretching vibration characteristic peak of Si-OH group<sup>11,13</sup>. The peak near 618 cm<sup>-1</sup> was the bending vibration characteristic peak of Si-OH group<sup>11,13</sup>. These peaks and groups would appear in all silica products.

**XRD pattern analysis:** XRD pattern was used to characterize the crystalline structure of material. There was no data on nano-silica in powder diffraction file of international centre for diffraction data. XRD pattern of small size nano-silica was shown in Fig. 2. The peak at 22.5° was the characteristic peak of the amorphous structure of nano-silica<sup>3,9</sup>. The intensity of the peak of nano-silica was very low. It suggested that nano-silica approached to crystal. It also indicated that nano-silica was steady. It was due to that SiO<sub>2</sub> was arrayed a tetrahedron and Si was located in the core of the tetrahedron and there are only -OH groups on the surface of nano-silica. This peak would appear in all silica products. The small peak at 32° may be caused by the impurity. The amorphous characteristic peak occurred at 2θ = 22° in nano-silica product<sup>9</sup>.

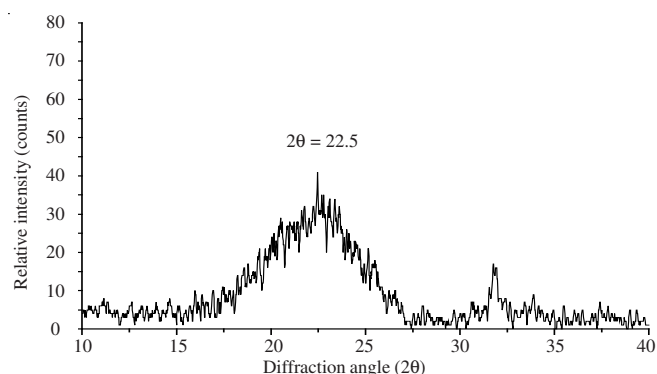


Fig. 2. XRD pattern of small size nano-silica

**TEM image analysis:** TEM image was always used to characterize agglomeration degree and morphology of particles. TEM image of small size nano-silica was shown in Fig. 3. Nano-silica in this study was agglomerative and the size was big. Water molecules in wet silica gel interacted with

the surface free hydroxyls of the gel particles through hydrogen bonds. When the gel particles got close, these molecules would draw neighbouring particles together. These bridging water molecules were removed when the gel began to dry and hydrogen bonds between the surface hydroxyls of two neighbouring particles would draw them closer. Further drying would cause the formation of strong chemical bonds between neighbouring particles. Then hard agglomeration appeared. The agglomeration principle of nano-silica was shown in Fig. 4.

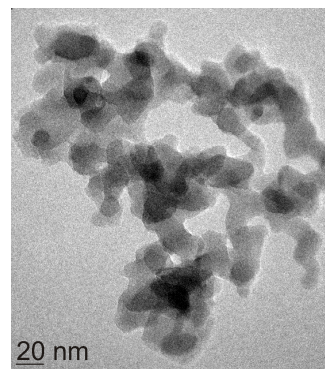


Fig. 3. TEM image of small size nano-silica (magnification: 50000 times)

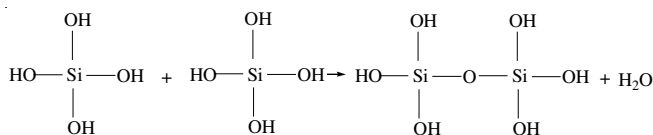


Fig. 4. Agglomeration principle of nano-silica

## Conclusion

This work made it clear that concentration of sodium silicate solution and adding speed of acid solution could affect the size of nano-silica. The size of nano-silica was small (30 nm) when the concentration of sodium silicate solution was 11.8 % and the adding speed of H<sub>2</sub>SO<sub>4</sub> solution (10 %, w/w) was 14.5 mL/min. FT-IR analysis indicated that the conduct contained all characteristic peaks and groups of silica. XRD pattern suggested that the amorphous characteristic peak of the product occurred at 2θ = 22.5°. TEM image revealed that the size was about 30 nm and the product was a little agglomerative.

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