

# Harvesting silica nanoparticles from rice husks

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**Abstract** Biogenic silica nanoparticles were synthesized using rice husks (RHs) as the raw material via controlled pyrolysis. The characterization results showed that the morphology of the synthesized silica was highly related to the pretreatment of RHs and the pyrolysis conditions. Particularly, potassium cations in RHs were found to catalyze the melting of silica, during which the amorphous silica were converted to crystalline phase. Two hours of pyrolysis at 700 °C appeared to be ideal to synthesize silica nanoparticles with a diameter of ca. 20–30 nm. Higher temperature and longer duration of pyrolysis led to undesired melting of silica nanoparticles, while too low a temperature cannot effectively remove carbonous residues. Such amorphous silica nanoparticles with narrow size distribution and high purity are expected to replace silica gel and fumed silica for various applications.

**Keywords** Silica · Rice husk · Nanoparticle · Amorphous · Biomaterials

## Introduction

Silica is a very important material and has been extensively used in a wide range of applications, including as ingredients in food, pesticides, and personal care products; as fillers in coatings, plastics, and rubbers; and as starting materials for semiconductors, silicates, and ceramics (Glasser 1986; Uhrlandt 2006). The application and value of various silica products are highly related to their crystallinity and microstructure. Crystalline silica is the most abundant material in the earth's crust, but owing to its low reactivity, the direct applications of crystalline silica are limited (Glasser 1986; Uhrlandt 2006). However, amorphous silica, particularly the ones with high surface area (porous and/or with a small particle size), are of high interest to many key chemical applications, such as absorbents, thermal insulators, and catalyst supports (Gurav et al. 2010; Pajonk 2003). Recently, silica for biomedical applications, such as controlled release and biosensors, have also been reported (Trewyn et al. 2007; Slowing et al. 2007).

So far, many approaches have been developed to synthesize silica nanoparticles. Usually, a silica precursor, like silicon alkoxides, is used as the silicon

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source (Soleimani Dorcheh and Abbasi 2008; Halas 2008; Vivero-Escoto et al. 2010). Silicon alkoxides (such as tetraethoxysilane) are typically synthesized from the carbothermal reduction of raw silica, such as sand (Rösch et al. 2000; Laine et al. 1991). Such chemical processes are energy intensive and thus expensive, and are also usually associated with high temperature, high pressure, and strong acidity, and thus eco-hazardous (Bansal et al. 2006). Considering the ever increasing demand on silica nanoparticles for new applications (Soleimani Dorcheh and Abbasi 2008; Vivero-Escoto et al. 2010), the current approach to synthesize silica nanoparticles may not be sustainable and match the cost requirement. Thus, it is highly desirable to seek an alternative approach that is more economical and environmentally benign.

Silicon is an important element, and sometime is even considered as a nutrition for many plants (Ding et al. 2005). It is well known that certain plants, including rice (*Oryza sativa*), grasses (*Gramineae*), horsetail (*Equisetum*), contain a high concentration of biogenic silica (Ding et al. 2005; Sun and Gong 2001; Sapei et al. 2008). The large abundance of silica in the earth crust is released into soil by chemical and biological processes, and absorbed by plants probably in the form of water-soluble silicic acid, which is subsequently polymerized and precipitated as amorphous silica (Lucas et al. 1993; Treguer et al. 1995; Derry et al. 2005; Bansal et al. 2006). The biosilicification process under mild physiological conditions generates a diversity of complex and hierarchical biogenic silica nano-structured frameworks, which contribute to the compression resistance and rigidity of cell walls (Mann 1993; Oliver et al. 1995; Mann and Ozin 1996; Ding et al. 2005). Compared to other plants, rice is particularly an ideal resource for biogenic silica, since the silica is mainly concentrated in rice husks (RHs), a byproduct of rice production. RHs typically contain 20–22 wt% total weight of rice grains (Bansal et al. 2006). In 2007, the estimated global rice production is ca. 650 million tons (FAO Statistics on rice production 2008). However, owing to their tough, woody, abrasive nature, low nutritive properties, great bulk, and high ash content, efforts to utilize RHs have been very limited, mostly in low-value applications in agricultural areas, or as fuel, or have to be disposed with additional cost, and even generating pollution issues (Sun and Gong 2001). Harvesting amorphous silica from RHs can not only

take full advantage of the highest possible value from RHs, but also minimize the related environmental issues associated with the current applications/disposals of RHs. Meanwhile, it may help open a completely new economical approach to synthesize valuable amorphous silica from a biomass, instead of the energy-intensive process currently adopted by industry.

In RHs, silica is in hydrated amorphous form (Asuncion et al. 2005) and counts up to ca. 20 wt% of dry husk, depending on the variety, climate, and geographic location (Umeda et al. 2007; Zhang et al. 2010; Liou and Wu 2010; Sun and Gong 2001). Attempts to extract silica from RHs have been explored by removing organic components in RHs via pyrolysis (Kapur 1985; Luan and Chou 1990; Real et al. 1996; Conradt et al. 1992; Patel et al. 1987), hydrothermal decomposition (Wu 1996), microbial fermentation (Rohatgi et al. 1987), or biotransformation process (Bansal et al. 2006). While the earlier study mainly focused on the purity of the obtained silica, much less emphasis was placed on the morphology of the silica from RHs. In this research, we managed to control the morphology and size of silica nanoparticles by tailoring the pretreatment and reaction conditions.

## Experimental

The RHs used in this research were obtained from Guangdong Academy of Agricultural Science. Analytical reagent grade hydrochloric acid (37 wt%),  $\text{Ca}(\text{NO}_3)_2$ , and  $\text{KNO}_3$  were purchased from Guangzhou Chemical Reagent Company and used as received.

Three approaches were adopted to treat RHs to obtain silica. In the first approach, raw RHs without any pretreatments were piled at an open field, then ignited and burnt naturally. The resulting RH ash is a mixture of off-white, gray, and black powders. Black color is contributed by the carbonous residues from the incomplete burning of organic components in RHs. Off-white RH ash with a tiny amount of gray/black particles were carefully collected, and hereafter referred to as RHS1. Overall, RHS1 exhibits a gray color after brief grounding. For the second approach, raw RHs were first rinsed with deionized water three times at room temperature to remove dusts and then dried at 100.0 °C for 24 h. The dried RHs were then

pyrolyzed in a muffle furnace which was preheated to a predetermined temperature (600, 700, or 800 °C) for certain time (1, 2, 4, or 8 h). For the third approach, raw RHs were boiled in 10 wt% HCl solution for 2 h, rinsed with deionized water, and then dried at 100.0 °C for 24 h. The dried RHs were then subjected to the same pyrolysis treatment as the second approach. The resulting samples from the second and third approach were hereafter referred to as RHS2-T-d and RHS3-T-d (T: pyrolysis temperature (600, 700, or 800 °C); d: duration of pyrolysis (1, 2, 4, or 8 h)), respectively.

Thermogravimetric analysis (TGA) of the dried RHs was carried out on a Perkin-Elmer TGS-2 thermogravimetric analyzer with a scan rate of 10 °C/min under air purge. X-ray diffraction (XRD) analysis was performed on a Rigaku D/MAX-III diffractometer with a monochromic copper  $K\alpha$  ( $\lambda = 0.1540$  nm) radiation source. The obtained silica samples from different approaches were grinded with KBr to prepare pellets for Fourier transform infrared (FT-IR) characterization, which was performed on a Perkin Elmer Spectrum One FT-IR spectrophotometer. Scanning electron microscopy (SEM) images were acquired on a JEOL JSM 6330F field emission-SEM (FE-SEM). The samples were sputter coated with a thin layer (ca. 3 nm) of Au/Pd before the SEM imaging. Energy-dispersive spectroscopy (EDS) analysis was performed on an Oxford INCA Energy EDS analysis system.

## Results and discussion

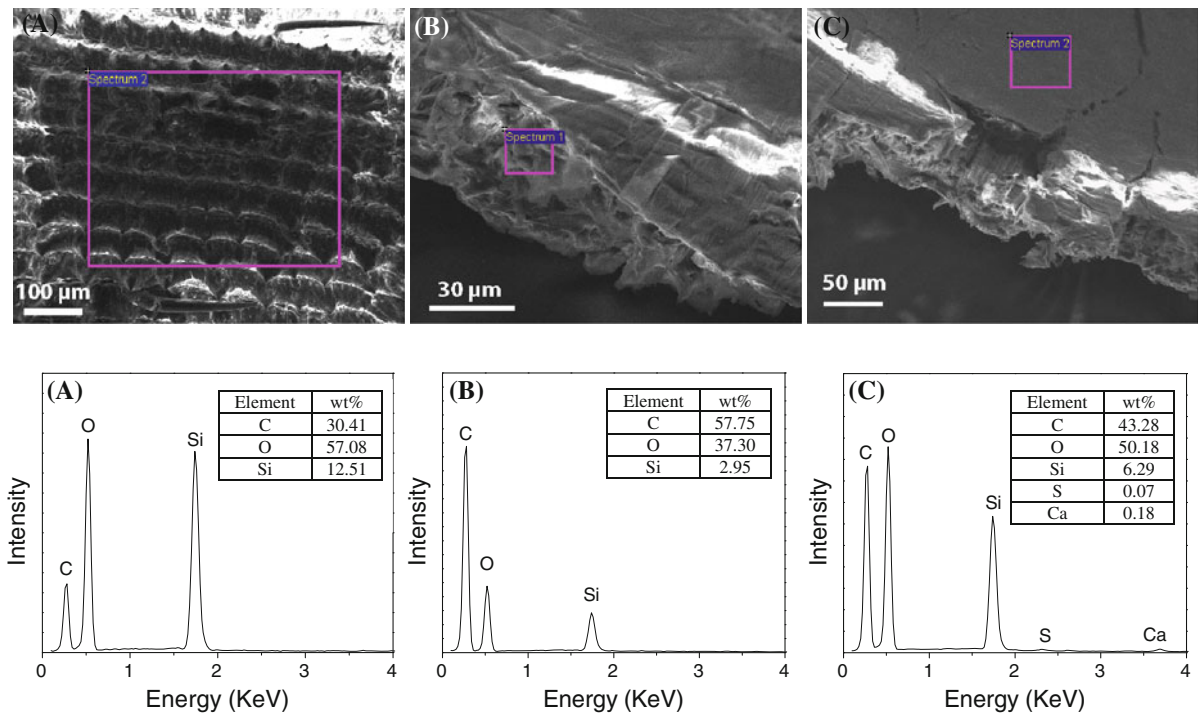
Like other biomasses, RHs are mainly composed of cellulose, hemicellulose, and lignin (Markovska and Lyubchev 2007; Teng and Wei 1998), in addition to hydrated silica (Sun and Gong 2001; Asuncion et al. 2005). Figure 1 shows the representative SEM images and corresponding EDS spectrum of the external surface, cross-section, and internal surface of a water-rinsed RH. As shown in the SEM image (Fig. 1a), the external surface of RH is covered with small irregularly shaped domes that are well aligned. Such domes are the reason that RHs feel abrasive. The EDS data show that the external surface contains ca. 12.51 wt% Si, which corresponds to ca. 26.76 wt% silica. The internal surface of RH (Fig. 1c) appears to be much smoother, and contains a much lower concentration of

silicon of ca. 6.29 wt% (corresponding ca. 13.46 wt% silica) according to the EDS characterization. The cross-section contains even lower concentration of silicon of ca. 2.95 wt%. Overall, the EDS characterization results on silica concentration show that the majority of silica is located at the two surfaces of RH, particularly the external surface.

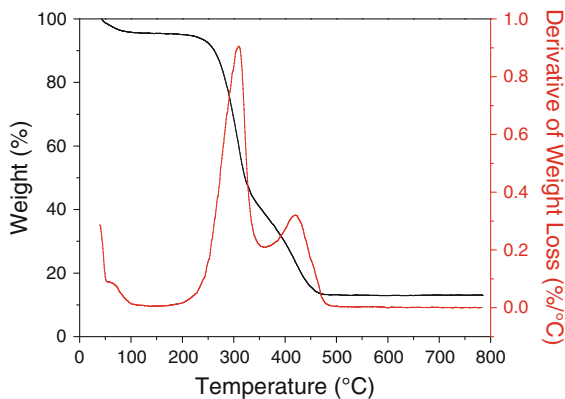
Since, cellulose, hemicellulose, and lignin can all be easily removed by thermal decomposition, pyrolysis of RHs at high temperature is a logic approach to collect silica from RHs (Sun and Gong 2001). To determine the ideal pyrolysis temperature, the RHs were initially analyzed by TGA under air. The TGA thermogram shows three steps of weight loss, as presented in Fig. 2. The weight loss (ca. 4.5 wt%) before 100 °C was the loss of water. From ca. 225 °C, cellulose, hemicelluloses, and lignin started to degrade quickly. After ca. 325 °C, RHs started to exhibit a third stage of weight loss, which can be attributed to the burning of the carbonous residues formed from the degradation of cellulose, hemicelluloses, and lignin (Markovska and Lyubchev 2007). After ca. 480 °C, there was virtually no weight loss up to 785 °C. The remaining weight (ca. 13.0 wt%) was most likely owing to the formation of silica. Based on the TGA results, 500 °C was initially selected as the starting pyrolysis temperature. However, the preliminary investigation showed that the pyrolysis at 500 °C was not sufficient to completely eliminate carbonous residue, generating samples with gray color. Thus, three temperatures, 600, 700, and 800 °C, were selected to pyrolyze RHs to obtain high purity silica.

It was expected that both temperature and duration of pyrolysis would affect the removal of organic components in RHs, thus a series of experiments were designed by varying both temperature and pyrolysis duration to obtain various silica samples. Roughly defined color of the obtained silica is summarized in Table 1 and the digital pictures of the representative samples are presented in Fig. 3.

Overall, the results in Table 1 suggest that a higher temperature and longer duration of pyrolysis lead to higher purity silica, considering the color is from the carbonous residue due to the incomplete decomposition of lignocellulose. Meanwhile, the acid treatment is much more effective than water rinse for improving product purity. The black impurities are carbonous residues from the incomplete burning of lignocellulose in RHs. As discussed in the “[Experimental](#)”



**Fig. 1** Representative SEM images (*top*) and corresponding EDS spectra (*bottom*) of external surface (**a**), cross-section (**b**), and internal surface (**c**) of RH



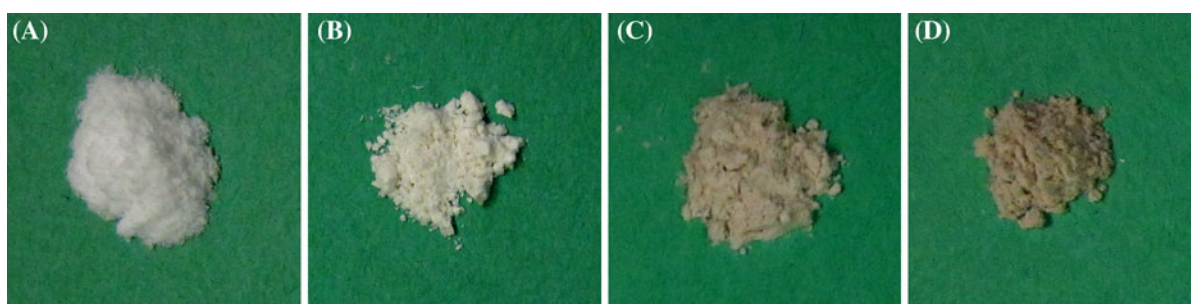
**Fig. 2** Weight loss curve and derivative of weight loss curve of water-rinsed RHs

section, RHS1 exhibited a gray color. At a relatively low temperature of 600 °C, for the water-rinsed RHs, even after 8 h of pyrolysis, there was still a tiny amount of residue left, leading to light gray appearance. Pyrolysis at a higher temperature (such as 800 °C) helped reduce the carbonous residue significantly but cannot completely eliminate them even after 8 h of treatment. While at a temperature of

800 °C, for the acid-treated RHs, 1 h of pyrolysis is sufficient to completely remove carbonous residue to generate silica with a high purity, as evidenced by its bright white color. Because of the intimate contact between silica and carbon in RHs (some of the silica might also be bonded to the organic compounds in RHs) (Sun and Gong 2001), it is reasonable to hypothesize that lignocellulose and hydrated silica intertwined, and thus a tiny amount of carbonous residues stay between neighboring silica particles or even within silica particle pores after initial degradation of lignocellulose. Either a longer treatment or a higher temperature can help further remove such carbonous residues. As will be discussed in detail later, RHs contain a tiny amount of potassium cations, which promote the melting of silica particles. For the water-rinsed RHs,  $K^+$  cations cannot be completely removed. During melting of silica, some carbonous residues were encapsulated within the silica crystal, which cannot be removed even after 8 h of pyrolysis at 800 °C. While for the acid-treated RHs,  $K^+$  cations were effectively removed. Silica thus remained virtually unmelted up to 800 °C, which allows the carbonous residues between silica particles or within pores

**Table 1** Color of the prepared silica samples

Sample	Color	Sample	Color	Sample	Color
RHS1	Gray	–	–	–	–
RHS2-600-1	Gray	RHS2-700-1	Gray	RHS2-800-1	Light gray
RHS2-600-2	Gray	RHS2-700-2	Light gray	RHS2-800-2	Light gray
RHS2-600-4	Gray	RHS2-700-4	Light gray	RHS2-800-4	Off-white
RHS2-600-8	Light gray	RHS2-700-8	Light gray	RHS2-800-8	Off-white
RHS3-600-1	Gray	RHS3-700-1	Off-white	RHS3-800-1	White
RHS3-600-2	Gray	RHS3-700-2	White	RHS3-800-2	White
RHS3-600-4	Off-white	RHS3-700-4	White	RHS3-800-4	White
RHS3-600-8	White	RHS3-700-8	White	RHS3-800-8	White

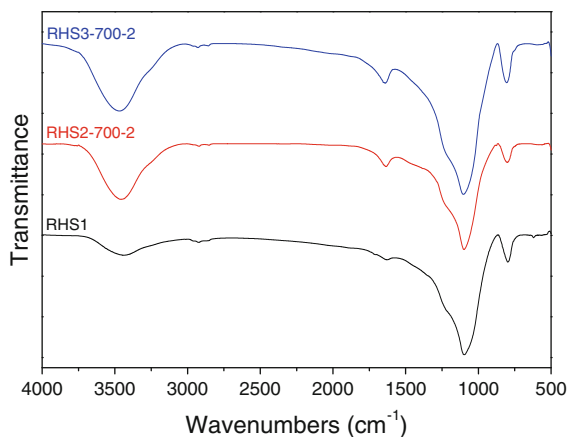
**Fig. 3** Representative silica samples exhibiting various colors: **a** RHS3-700-2 (*white*); **b** RHS3-600-4 (*off-white*); **c** RHS2-800-2 (*light gray*); and **d** RHS2-600-2 (*gray*)

to be completely removed, and thus generating high purity silica. Pyrolysis at temperatures higher than 800 °C may help remove carbonous residues, but it also results in the formation of crystalline silica (will be discussed later), which is not desirable for most applications. Meanwhile, higher temperature means higher energy consumption. Considering the ultimate goal is to obtain high quality silica from RHs at the lowest possible cost, pyrolysis at temperatures higher than 800 °C is not included, and the following discussions will focus on the conditions leading to high purity samples.

Selected silica samples were characterized by FT-IR, and their spectra are presented in Fig. 4. The broad peak at ca. 3,200–3,600  $\text{cm}^{-1}$  corresponds to the stretching vibrations of hydroxyl groups (Martinez et al. 1998), while the band at 1,630–1,640  $\text{cm}^{-1}$  is the deformation mode of water molecules absorbed on the silica particle surface (Martinez et al. 1998). The peaks at ca. 800 and 1,100  $\text{cm}^{-1}$  are the bending and stretching vibration of  $\text{SiO}_2$  lattice, respectively

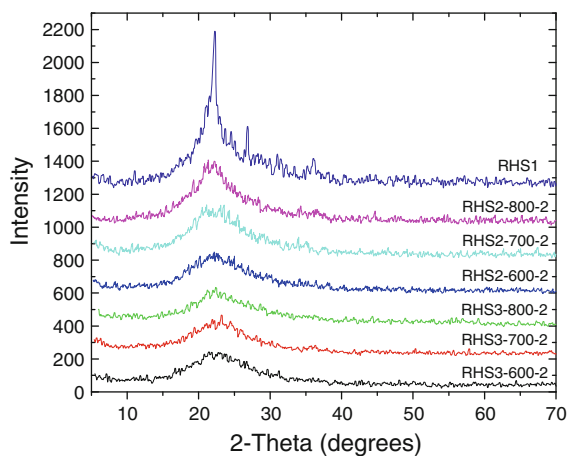
(Bansal et al. 2006; Martinez et al. 1998). To be noted, the peaks centered at ca. 1,100  $\text{cm}^{-1}$  show obvious broadening and a shoulder at the high wavenumber side of the stretching in the 1,160–1,290  $\text{cm}^{-1}$  range. This can be attributed to the asymmetric stretching vibrations of the tetrahedral  $\text{SiO}_4$  coordination units (Pol et al. 2003; Martinez et al. 1998; Schraml-Marth et al. 1992), which suggests the formation of Q4 units instead of Q3 or Q2 units in the silica samples (Schraml-Marth et al. 1992; De et al. 1993). The similar spectra of the three silica samples indicate that the pretreatment does not affect the chemical structure of the synthesized silica.

It is generally accepted that silica in RHs is predominantly in inorganic linkages and in amorphous phase (Sun and Gong 2001). After pyrolysis, silica exists in various levels of crystallinity depending on the pretreatment and pyrolysis conditions. Overall, the results showed that the uncontrolled combustion of raw RHs generated a mixture of amorphous and crystalline silica (RHS1), as evidenced by the sharp



**Fig. 4** FTIR spectra of the silica samples obtained from different conditions

diffraction peak imposed on a broad hump as shown in Fig. 5. The position of the diffraction peak indicated that the crystalline silica is cristobalite (San and Özgür 2009). Rinsing RHs with water helps lower the crystallinity of the prepared silica significantly, while the treatment with HCl turned to be even more effective. Meanwhile, the HCl-treated RHs appeared to be much less sensitive to pyrolysis temperature compared to the water rinsed ones. For example, 2 h pyrolysis of HCl-treated RHs at a temperature up to 800 °C still resulted in amorphous silica (RHS3-800-2). However, the silica obtained from the water-rinsed RHs started to exhibit certain level of crystallinity when the pyrolysis temperature was raised to 700 °C (RHS2-700-2), and exhibit even higher crystallinity

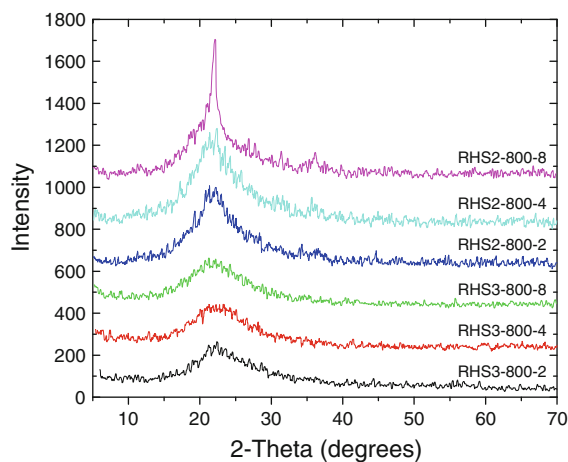


**Fig. 5** XRD patterns of silica obtained from various pretreated RHs under different pyrolysis conditions

when the pyrolysis temperature was increased to 800 °C for 2 h (RHS2-800-2).

By extending the duration of pyrolysis, the above trend turned to be even more obvious, as shown in Fig. 6. For the HCl-treated RHs, even after 8 h of pyrolysis at 800 °C (RHS3-800-8), the resulted silica remained to be amorphous. However, at the same temperature of 800 °C, 2 h of pyrolysis of water-rinsed RHs (RHS2-800-2) already generated silica samples with certain level of crystallinity according to its diffraction pattern. Further extending pyrolysis time led to much higher level of crystallinity.

The SEM images of the synthesized silica are shown in Fig. 7. The top three images (Fig. 7a, b, and c) show representative morphologies of silica obtained from natural combustion of non-treated RHs. Two typical morphologies were observed: completely melted silica (Fig. 7a) and partially melted silica forming irregular porous structure (Fig. 7c), while Fig. 7b shows the transition between the two. The results indicated that with increasing temperature, silica particles started to melt and gradually fused together. Since, the RHs went through uncontrolled combustion, certain regions reached silica melting temperature and maintained at melting state long enough, which allowed the melt to merge. Upon cooling, they form crystalline silica. The small pinholes on the top surface of the crystalline silica as shown in Fig. 7a represent the remaining traces of the merge of silica clusters. While for certain regions, owing to insufficient heat supply, it started to cool



**Fig. 6** XRD patterns of silica obtained via various calcination temperature and durations

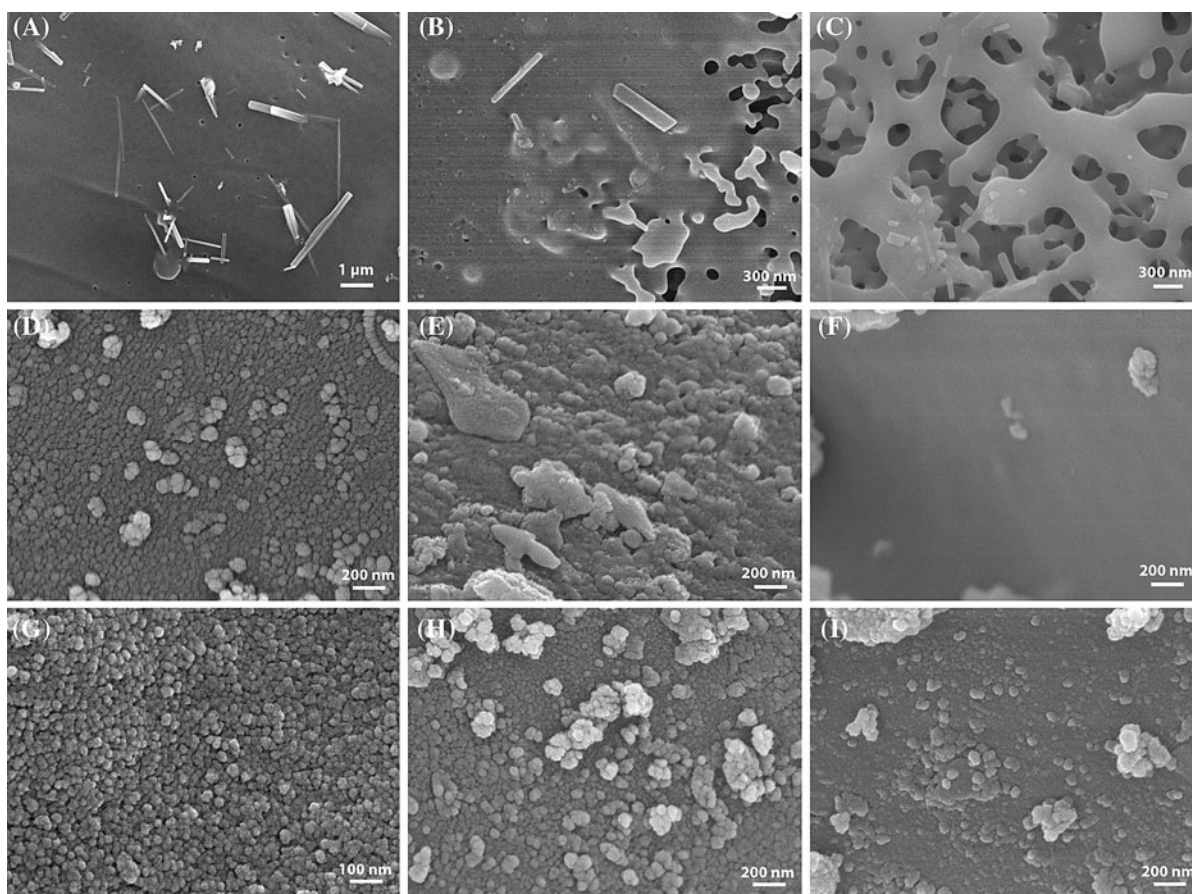
down before silica completely melted and fused. This led to irregular porous structure. It should be noted that RHS1 was collected from the off-white ashes located at the center of RH ash pile after uncontrolled combustion, where highest combustion temperature was reached. The ashes located at the edge of the pile exhibited black or gray color, which indicated incomplete combustion of RHs and remaining of carbonous residues.

Figure 7d, e, and f present the morphology of RHS2-700-2, RHS2-800-2, RHS2-800-8, respectively. As the images clearly show, after 2 h of pyrolysis at 700 °C, the water-rinsed RHs were converted to fine silica particles with a diameter ranging from ca. 30 to 80 nm. However, pyrolyzing at a higher temperature of 800 °C for 2 h led to significant melting of silica nanoparticles, resulting in aggregates. Extending pyrolysis at 800 °C to 8 h led to complete melt of silica. The morphologies of silica

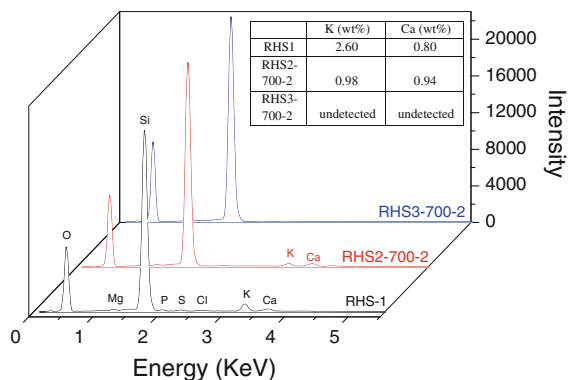
samples shown in SEM images are consistent with their crystallinity characterized by XRD as shown in Figs. 5 and 6.

Ultrafine silica nanoparticles were successfully obtained by pyrolyzing HCl-treated RHs at 700 °C for 2 h (RHS3-700-2). Silica nanoparticles with narrow size distribution of ca. 20–30 nm are shown in Fig. 7g. Upon increasing pyrolysis temperature to 800 °C, silica nanoparticle clusters were observed, indicating the start of the melting of silica among some of the particles (Fig. 7h). Extending pyrolysis at 800 °C to 8 h further promoted the melting, resulted in even larger clusters. However, in contrast to RHS2 series of samples, only certain regions melted; some particles remained intact (Fig. 7i). Again, the particle morphologies shows high agreement with their crystallinity as discussed above.

The melting temperature of pure silica is typically above 1,600 °C without the presence of catalyst



**Fig. 7** SEM images of silica samples: RHS1 (a, b, c), RHS2-700-2 (d), RHS2-800-2 (e), RHS2-800-8 (f), RHS3-700-2 (g), RHS3-800-2 (h), and RHS3-800-8 (i)

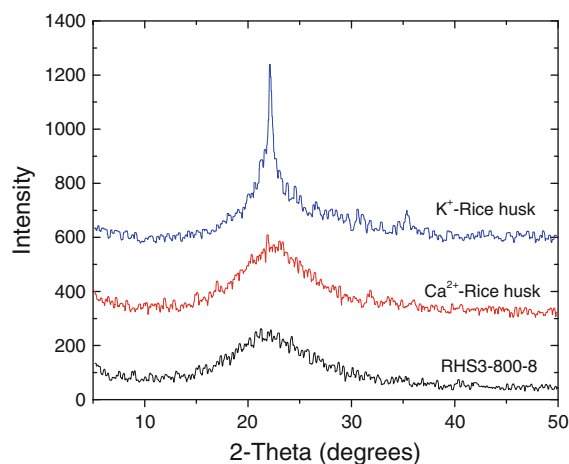


**Fig. 8** Elemental analysis of RHS1, RHS2-700-2, and RHS3-700-2 silica samples

(Haynes 2010). The fact that the silica samples from untreated RH and water-rinsed RHs tended to melt much more significant than the ones from HCl-treated RHs indicates that the melting of silica is possibly initiated by certain catalyst(s) contained in RHs, which can be effectively removed by HCl but not water. The observation of partial melting of silica after 8 h of pyrolysis of HCl-treated RHs at 800 °C further indicated that HCl treatment can remove most catalyst(s), but a trace amount of catalyst(s) might still remain, which catalyze the melting of silica nanoparticles regionally.

To identify such catalyst(s) in RHs, three selected silica samples, RHS1, RHS2-700-2, and RHS3-700-2 were subjected to elemental analysis. The results, as presented in Fig. 8, show that RHS1 contained a number of elements other than C, O, and Si, including Mg, P, S, Cl, K, and Ca. After water rinse, most of the impurities were removed; the obtained RHS2-700-2 sample contained Ca and K as the main impurities. Water rinse can partially remove  $K^+$  cations, but had little effect on  $Ca^{2+}$  cations. Pretreatment with HCl appears to be very effective to remove contaminants. Other than C, O, and Si, no other elements were detected in sample RHS3-700-3. Since, severe melting of silica nanoparticles were observed in water-rinsed samples as shown in Fig. 7,  $Ca^{2+}$  and/or  $K^+$  cations might be the catalyst(s) that promote the melting of silica nanoparticles according to the elemental analysis.

To prove the above hypothesis and identify which ones indeed catalyze the melting of silica in RHs, two samples of RHs were first boiled in 10% HCl for 2 h to remove the majority of impurities, and then rinsed



**Fig. 9** XRD patterns of silica samples obtained from 8 h of calcinations at 800 °C of  $Ca(NO_3)_2$  and  $KNO_3$ -treated RHs

with deionized water and dried at 80.0 °C for 24 h. One of the dried sample was stirred in 0.10 M  $Ca(NO_3)_2$  solution for 2 h, while the other was stirred in 0.10 M  $KNO_3$  solution for 2 h. After brief rinse with water, both of the two samples were filtered and dried in an oven at 80.0 °C for 24 h. The dried samples were pyrolyzed at 800 °C for 8 h, with an intention to promote the potential melting. The resulted silica samples were characterized by XRD and their patterns are shown in Fig. 9. The results clearly show the formation of cristobalite in the  $KNO_3$ -treated sample, similar to the patterns of RHS1 and RHS2-800-8 as shown in Figs. 5 and 6, respectively. While no crystalline phase formed in the  $Ca(NO_3)_2$ -treated sample, which remained to be amorphous and exhibited a pattern similar to that of RHS3-800-8. The above results confirmed that  $K^+$  is the catalyst which promotes the melting of silica nanoparticles, while  $Ca^{2+}$  has little catalytic effect. Similar phenomena on the interactions between  $K^+$  cations and silica, and disruption of  $SiO_4$  network by  $K^+$  cations have also been reported in other systems (Bassett et al. 1972; Kamijo and Umesaki 1993; Huffman et al. 1995; Real et al. 1997).

## Conclusions

Biogenic silica nanoparticles were successfully prepared from RHs via controlled pyrolysis. Both the pretreatment of RHs and the pyrolysis conditions are critical for the preparation of silica nanoparticles.



In particularly, potassium cations were identified as catalyst which promoted the melting of silica, leading to the formation of crystalline silica bulks. Two hours of pyrolysis at 700 °C appeared to be ideal to generate silica nanoparticles with a diameter of ca. 20–30 nm from HCl-treated RHs. Such silica nanoparticles with high purity are expected to be able to replace silica gel or fumed silica for many applications. Finally, the elemental analysis showed that such silica nanoparticles from RHs containing low concentrations of aluminum and iron, the two major impurities affect the production of high purity silicon (Amick 1982; Hunt et al. 1984). Thus, they may also potentially be used to synthesize high purity silicon for solar cell applications at a lower cost.

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