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Preparation and characterization of nanosilica from rice husk ash by chemical treatment combined with calcination

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Abstract

This work presented the results of the study on synthesis and characterization of nanosilica from rice husk ash (RHA). Nanosilica was obtained by calcination of HCl treated RHA at 700 ^oC for 2 h. X-ray diffraction (XRD) pattern showed only one peak at $2\theta \sim 22^o$ confirming the amorphous structure of nanosilica. The chemical composition assessed by energy dispersive X-ray spectroscopy (EDX) showed that the obtained nanosilica was of high purity. TEM image measured by transmission electron microscopy (TEM) revealed that the obtained nanosilica was in spherical morphology with the average diameter of about 45.5±7.2 nm. The particle size distribution of nanosilica determined by dynamic laser scattering (DLS) was of Gaussian mode. The FTIR spectrum indicated the presence of silanol and siloxane groups in nanosilica. Thus, the synthesized nanosilica can be used for application in different fields.

Keywords. Rice husk ash, nanosilica, amorphous.

1. INTRODUCTION

Nanotechnology has attracted considerable scientific interest due to the potential uses of the nanomaterials and nanocomposite. There are several reports on synthesized nanosilica used in vegetable oil refining, as medicines, detergents, adhesives, ceramics, and pesticide [1, 2]. Tetraethoxysilane (TEOS) and tetramethoxysilane (TMOS) have been usually used as the silica source to produce nanosilica [1]. However, these chemical sources are rather expensive and toxic. Rice husk ash (RHA), rich in silica of about 83-90 % is one of the waste products [1, 3]. Typically, the major remaining inorganic component of Vietnamese RHA is SiO_2 (96.15 %), along with some minor inorganic constituents including aluminium oxide (0.48 %), iron oxide (0.15 %), calcium oxide (0.73 %), magnesium oxide (0.55 %), sodium oxide (0.12 %), potassium oxide (0.39 %), and a loss of ignition (1.43 %) [4]. Various methods for preparing nanosilica from rice husk (RH) have been reported in the literature, such as sol–gel [4, 5], precipitation [6-8], and pyrolysis method [3, 9-14]. The world's most researching synthesis of nanosilica from RH is that metal oxides were removed from RH by treatment with acid, then silica was extracted by alkaline (NaOH), precipitated with acid and finally calcined at high temperature to obtain nanosilica [3,5,11]. The reaction processes are described as follows:

$$SiO_2\,(ash) + 2NaOH \rightarrow Na_2SiO_3 + H_2O \quad (1)$$

$$Na_2SiO_3 + H_2SO_4 \rightarrow SiO_2\downarrow + Na_2SO_4 + H_2O \quad (2)$$

Besides, many authors also studied a simple synthesis process that metal oxides were removed from RH by treatment with acid (HCl, H_2SO_4, organic acids) and then nanosilica was obtained by calcination of acid treated RH at temperature from 500 to 800 ^oC [9, 12, 13, 15]. There is also a recyclable method to obtain silica from RHA by using NH_4F that dissolved SiO_2 and precipitated SiO_2 by NH_3 [16]. The silica powder was obtained by the following reactions:

$$6NH_4F + SiO_2\,(RHA) \rightarrow (NH_4)_2SiF_6 + 4NH_3 + 2H_2O \quad (3)$$

$$(NH_4)_2SiF_6 + 4NH_3 + (n+2)\,H_2O \rightarrow 6NH_4F + SiO_2\downarrow + nH_2O \quad (4)$$

In Vietnam, Le *et al.* studied on synthesis of nanosilica by the sol–gel method [4]. Silica from RHA was extracted by sodium hydroxide to produce

sodium silicate solution and then silica was precipitated from sodium silicate solution by adding H_2SO_4 in the mixture of water/butanol and finally the precipitate was calcinated at 550 °C for 4h in atmospheric condition to obtain nanosilica. Nguyen *et al.* also prepared nanosilica from RHA by precipitation method [8]. Silica was extracted by sodium hydroxide solution and after that silica was precipitated with HCl solution.

In this paper, we present a process for synthesizing nanosilica from RHA for us as an agent for growth stimulation and disease resistance for plants. Nanosilica was synthesized from RHA by two steps. In the first step, metal oxide impurities were removed from RHA by treatment with acid. In the second step, the acid treated RHA was calcined at 700 ^oC.

2. EXPERIMENTAL

2.1. Materials

Rice husk from Dong Nai province, Vietnam was burned in open environment to collect RHA. HCl acid was purchased from Merck, Germany. Distilled water was used in all experiments.

Figure 1: Schematic illustration of the synthesis mechanism for nanosilica powder from rice husk ash

2.2. Preparation of nanosilica

5.0 g of RHA was stirred with 30 mL of 1N HCl for 2h at 80 ^oC and let standing overnight to remove metal ions in RHA [3, 12]. Then, acid treated RHA was filtered, washed with distilled water and dried at 110°C in an electric oven. The acid treated RHA was then calcinated in a programmable furnace (Nabertherm GmbH, Germany) at 700 ^oC for 2 h to obtain nanosilica [3, 9, 14]. The schematic illustration of the synthesis process of nanosilica was described in Fig. 1.

2.3. Characterization of nanosilica

The functional groups of the SiO_2 nanoparticles were analyzed by FT-IR technique. Spectral-grade KBr powder was mixed with nanosilica at a weight ratio of 2 mg SiO_2: 200 mg KBr in an agate mortar. The mixture powder was pressed into pellets with a diameter of 13 mm and thickness of 0.5 mm. The infrared (IR) spectrum of nanosilica was measured by using FTIR spectroscopy (FT-IR 8400S, Shimadzu) over the wavenumber range from 4000 to 400 cm^{-1}.

X-ray diffractometer (D8 Avance Bruker, Germany) was used to determine the amorphous phase of nanosilica. The XRD pattern was obtained by using CuKα as a radiation source (λ = 1.5405 Å) operating under a constant current of 30 mA at 40 kV with a diffraction angle (2θ) scan range from 5 to 80°.

The morphology and particle size of the nanosilica were measured using a transmission electron microscope (TEM) (JEM1010, JEOL, Japan). Silica particle size was statistically calculated from TEM image by Photoshop CS6 and Microsoft EXCEL 2010 softwares.

Dynamic light scattering (DLS) analysis of nanosilica was also performed using a Nano-Particle Size Analyzer (HORIBA, LB550, Japan).

The chemical composition of nanosilica was assessed by energy dispersive X-ray spectroscopy (EDX) on a JEOL 6610 LA.

3. RESULTS AND DISCUSSION

The inorganic metallic ions impurities in RHA were separated into the liquid by HCl leaching RHA suspension. After acid treatment, the organic constituents and silica remained as solid ingredients. The chemical reaction along with the high-temperature calcination for the preparation of nanosilica powder can be described as follows:

$$RHA + HCl \xrightarrow{80^oC\ (2\ h),\ soaked\ overnight} SiO_2\ (Ash) + MCl + H_2O \quad (5)$$

Where M: Na; K; Ca; Fe; Al, Mg,…

$$SiO_2\ (Ash) \xrightarrow{700\ ^oC\ (2\ h)} SiO_2\ (nanosilica\ powder) \quad (6)$$

During the high temperature calcinating process, all of the organic constituents were burned out. Finally, white powder nanosilica was obtained (Fig. 1).

The chemical composition of silica analyzed by EDX was presented in Fig. 2. As shown in Fig. 2, nanosilica contains only silicon and oxygen with weight ratio of about 1:1.5. This result confirmed that the obtained nanosilica is in good stoichiometric ratio and high purity. The elements such as Ca, K, Na, Mg, Fe, Al, and Mg.that were reported in composition of RHA were not detected in nanosilica obtained by calcination of acid treatment of RHA [3, 5, 8, 12, 14].

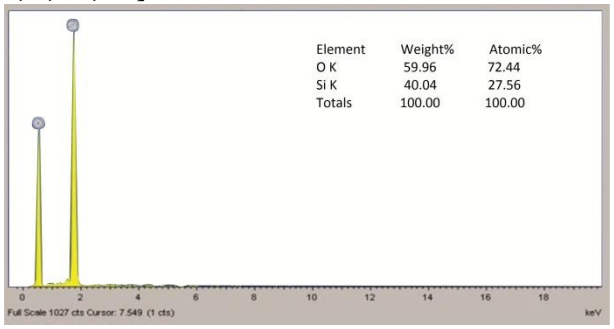

Figure 2: EDX spectrometric data of nanosilica produced from RHA

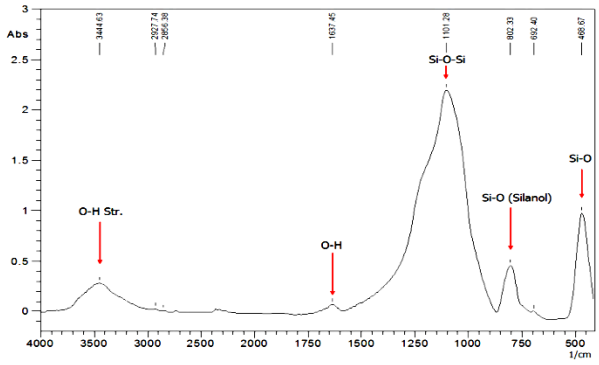

Figure 3: FT-IR spectrum of nanosilica from RHA

The FT-IR spectrum and FT-IR spectral data of nanosilica were shown in Fig. 3 and Table 1, respectively. The peaks at 468 and 802 cm^{-1} assigned to the rocking bond and symmetric bond vibrations of the Si–O (silanol), respectively. The peak at 1101 cm^{-1} is related to the vibrational stretching of asymmetric Si–O–Si in S1O4 tetrahedron [3], showing a stoichiometric silicon dioxide (SiO_2) structure. The O–H bending and stretching vibration modes also appeared in the absorption band region at 3444 and at 1637 cm^{-1}, respectively.

Table 1: FT-IR spectral data of nanosilica from RHA

Frequency (cm^{-1})	Position assignment	Literature value	References
468	Si–O bond rocking	438-475	[3, 4, 6, 8, 10, 11, 14, 17]
802	Symmetric Si–O bending (silanol)	796-805	[3, 4, 6, 10, 11, 14, 17]
1101	Asymmetric Si–O–Si stretching in S1O4 tetrahedron	1050-1150	[3, 4, 6, 10, 11, 14, 17]
1637	O–H bending	1633-1643	[3, 4, 8, 10]
3444	O–H stretching and adsorbed water	3437-3456	[3, 4, 8, 10, 11, 17]

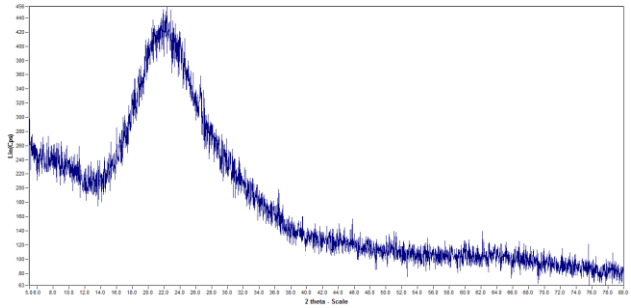

Figure 4: XRD diagram of silica from RHA

The XRD pattern of the obtained nanosilica in Fig. 4 showed only a single peak at 2θ ~22° which confirmed the amorphous structure of nanosilica [3, 4, 6, 11, 14-18].

The TEM image and particle size distribution of nanosilica were shown in Fig. 5. It can be observed from Fig. 5 that the obtained nanosilica was almost in spherical morphology with the average diameter of about 45.5±7.2 nm and the particle size distribution was in a fairly narrow range of 30-60

nm. The size of nanosilica obtained in this work was almost the same that of nanosilica synthesized from RH by other authors [3, 6, 8-11].

The size and particle size distribution of prepared nanosilica were also determined by DLS (Fig. 6). The results showed that particle size of nanosilica was in the range of 200-400 nm and the distribution was of Gaussian mode. Thus, the size of nanosilica from TEM image seems to be usually smaller than that from DLS [12].

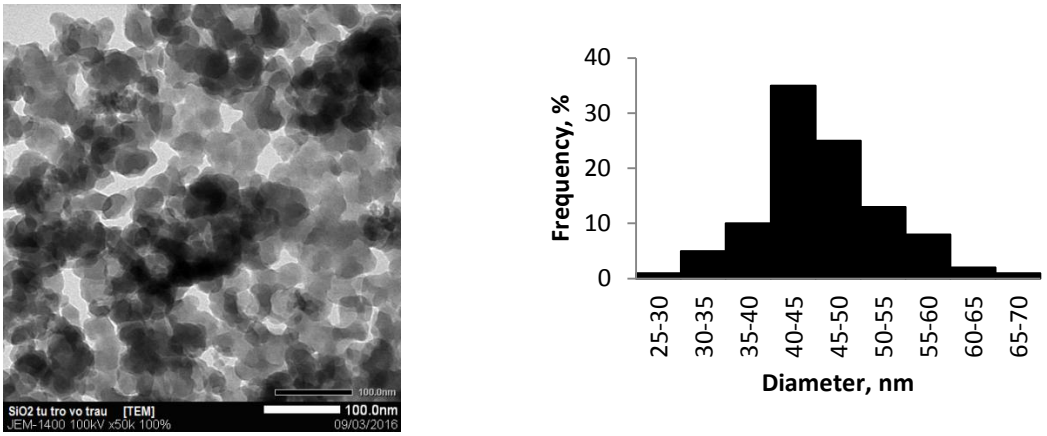

Figure 5: TEM images and distribution of particle size of nanosilica

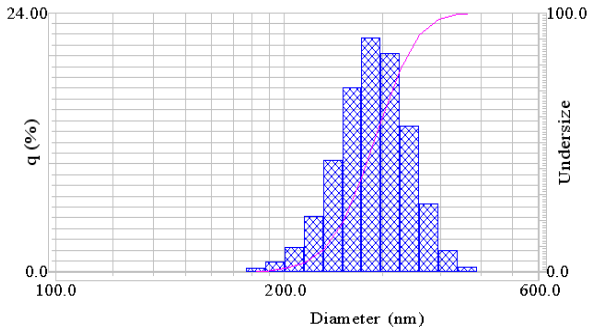

Figure 6: Distribution of particle size by DLS

Based on the results obtained, the method of synthesis of nanosilica from RHA is considered as an economical and suitable method for production of nanosilica on large scale for different applications.

4. CONCLUSION

In this study, a source attempt has been made to use cheap RHA to synthesize nanosilica with diameter of about 45.5 nm and narrow particle size distribution by acid treatment combined with calcination. This method is considered as a suitable and economical method to produce nanosilica on large scale. The obtained nanosilica can be applied in various fields and helps to minimize the concerns of RHA disposal.

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