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Pyrolysis method of gel SiO_2/chitosan for the preparation amorphous silica nanoparticles from waste rice husk ash

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ABSTRACT

Rice husk ash (RHA) is obtained from industrial waste from drying manufacture and easily available in Vietnam. However, for commercial viability, and for many applications, the pyrolysis method of SiO_2/chitosan gel to prepare silica nanoparticles with small particle size (< 10 nm) should not only be as efficient as possible but also adjustable particle size. This study characterized the elemental composition, crystallinity, size and morphology of silica nanoparticles obtained from industrial waste RHA was surveyed by Energy-dispersive X-ray, X-ray diffractograms and Transmission electron microscope. Silica nanoparticles have average diameter of about 9.0 ± 1.9 nm, narrow particle size distribution, high silica content of 99.56% and almost amorphous structure which has one peak at 2θ ~22.1°. Silica nanoparticles separated which may be due to the presence of hydrogen bonding between silanol groups of silica and –OH groups on the surface of chitosan. Fourier Transform Infra-Red spectra confirmed the presence of –OH groups and O-Si-O bonds of silica nanoparticles.

Introduction

Rice husk ash (RHA) rich in silica 84.3-98.61%, which is one of the industrial waste products of drying manufacturers [1,2]. Typically, the major remaining inorganic component of Vietnamese RHA is SiO_2 (90.13%), along with some minor inorganic constituents including alumina oxide (0.45%), iron oxide (0.17%), calcium oxide (0.83%), magnesium oxide (0.52%), sodium oxide (0.18%), potassium oxide (0.39%), and a loss of ignition (1.43%) [3]. Synthesis of silica nanoparticles with different particle sizes from rice husk ash is often a key step in many important apply targets such as catalysts, medicines, construction, and agriculture [4]. There are various types of methods for the synthesis of silica nanoparticles from rice husk ash such as the thermal method [5,6], alkaline extraction [4,7]. The procedure to be applied depends upon the morphology of the material, particle size, and surface area. The world's most researching synthesis of silica nanoparticles from RHA is that metal oxides were removed by acid (HCl, H_2SO_4,..), silica was extracted by alkaline (NaOH) and then precipitated silica with acid (inorganic or organic) [8] and finally calcination to prepare silica nanoparticles [4,7,9]. Besides, many authors also studied simpler synthesis processes that

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metal oxides were removed from RHA by treatment with acid, and then silica nanoparticles were obtained by calcination of acid-treated RHA at the temperature from 500 to 800°C [5,10-12]. However, the above studies only synthesized silica nanoparticles with a large particle size of 20-100 nm and agglomerated particles [9,12,13]. Therefore, to improve silica nanoparticles material with small size (<10 nm) and separated particles, we present a process for synthesizing silica nanoparticles from industrial waste rice husk ash to use the obtained silica nanoparticles as an agent for stimulation a growth and disease resistance for plants. Silica nanoparticles were synthesized from industrial waste RHA by third steps. For the first step, SiO_2 extracted from rice husk ash by NaOH obtained Na_2SiO_3. In the second step, SiO_2/chitosan gel formed between Na_2SiO_3 and chitosan solution. For the end step, SiO2/chitosan gel was calcined at 700°C in 2 hours.

Experimental

Materials

RHA waste from industrial drying manufactures at Dong Nai province, Vietnam, chitosan (degree of deacetylation ~ 94%; molecular weight ~ 100.000 $g.mol^{-1}$) provided by Institute of Applied Materials Science (HCMC, Vietnam), HCl was purchased from Merck, Germany, deionized water was used in all experiments.

Preparation of nano silica

Dissolve 60 g of waste rice husk ash (SiO_2 content ~ 85%) in 400 mL 1N NaOH solution, stir at 80°C for 2 hours, filter, and remove residue on filter paper to collect Na_2SiO_3 solution. Determine the SiO_2 content in the solution is 12% (w/v). Preparation of 50 mL of Na_2SiO_3 solution with SiO_2 (w/v) contents of 4%. Take 2.2 g of chitosan into 40 ml of 2% lactic acid solution, stir for 15 minutes and soak for 2 hours. Continue stirring for 2 hours at a temperature of 50°C, filter out sediment with stainless steel mesh (200 mesh hole size). Add 4.93 g of 37% HCl to the chitosan solution and add deionized water to obtain 50 mL of 4% chitosan solution. Then slowly, small, stir 50 mL of the prepared Na_2SiO_3 solution into a beaker containing 50 mL of 4% chitosan solution. Stir the mixture for 10 minutes. Using 1N NaOH to drip to adjust pH ~ 6, the SiO_2/chitosan gel was obtained with a SiO_2/chitosan mass ratio of 1/1. Cut up SiO_2/chitosan gel with size about 5 x 5 mm and wash and remove H^+ and OH^- ions with 98 alcohol/water mixture ~ 50/50 (w/w). Pyrolysis of SiO_2/chitosan gel for 2 hours at a temperature of 700°C by the Nabertherm oven (Germany) obtained silica nanoparticles powder.

Characterizations of silica nanoparticles

The functional groups of the silica nanoparticle were analyzed by the FT-IR technique. Spectral-grade KBr powder was mixed with silica nanoparticles at a weight ratio of 2 mg SiO_2:200 mg KBr) in an agate mortar. The powders were pressed into pellets with a diameter of 13 mm and thickness of 0.5 mm. The infrared (IR) spectra of silica nanoparticles were obtained by using FTIR spectroscopy (FT-IR 8400S, Shimadzu) over the wavenumber range from 4000 to 400 cm^{-1}. The field emission scanning electron microscopy (FE-SEM) with energy dispersive X-Ray (EDX) (Ultra, Zeiss, Germany) was used to determine the elemental composition of the silica nanoparticles. X-ray diffractometer (D8 advanced: Bruker, Germany) was used to determine the amorphous phase of silica nanoparticles. The X-ray Powder Diffraction (XRD) pattern was obtained by using CuKα1 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 of 10 to 80°. The morphologies and particle sizes of the silica nanoparticles were measured using a transmission electron microscope (TEM) (JEM1010, JEOL, Japan). Silica particle size was statistically calculated by software Photoshop CS6 and Microsoft EXCEL 2013.

Results and discussion

Morphology and particle size of silica nanoparticles

Silica nanoparticles were synthesis by pyrolysis of SiO_2/chitosan gel. The SiO_2/chitosan gel was prepared illustrated in the following chemical reaction equations (1) and (2) [9,11,14,]. Chitosan is a template for separating silica nanoparticles formed during the pyrolysis of SiO_2/chitosan gels. During the high-temperature calcination process, chitosan removed from the silica nanoparticles. Finally, white powder silica nanoparticles obtained (Figure. 1).

$$SiO_2 + 2NaOH \longrightarrow Na_2SiO_3 + 2H_2O \quad (1)$$

$$Na_2SiO_3 + Chitosan/H^+ \longrightarrow SiO_2/chitosan\ gel + Na^+ + H_2O \quad (2)$$

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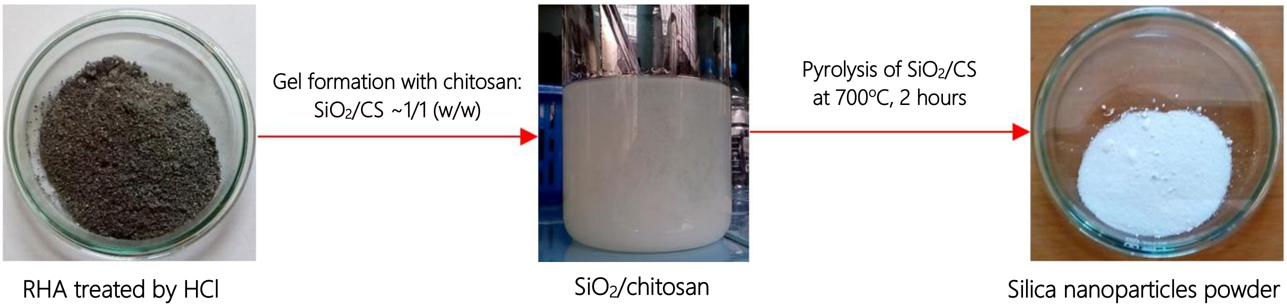

Figure 1: Simulation of the preparation process of silica nanoparticles by SiO_2/chitosan gel pyrolysis

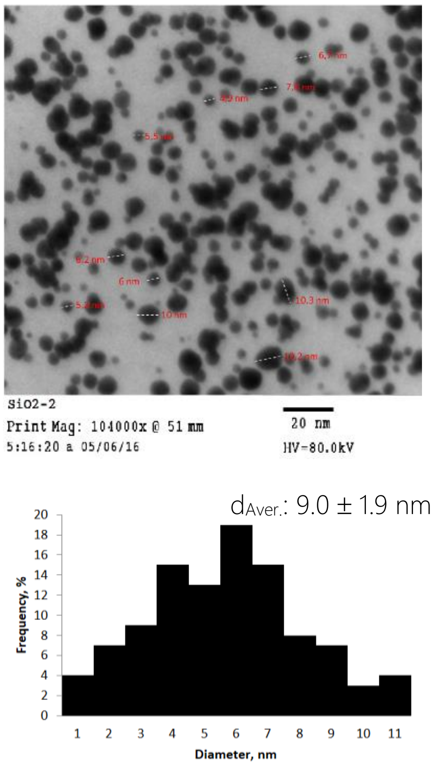

Figure 2: TEM images and distribution of particle size of silica nanoparticles from industrial waste RHA

TEM images and distribution of particle size of silica nanoparticles were showed in Fig. 2. The TEM image shows spheroidal-shaped particles composed of tiny nanoparticles that are 1 – 11 nm in size. Silica nanoparticles are an average diameter of about 9.0 ± 1.9 nm and narrow particle size distribution. Chun et al. reported the sol-gel synthesis of silica nanoparticles from rice husk using a template-free approach [4]. They simply titrated sodium silicate, which was obtained from rice husk ash, and used not template molecules. Their pH was adjusted with acid until the pH reached 7.0, was aged for 24 h. While V. H. Le et al. reported the synthesis of silica nanoparticles from rice husk using a template (Cetyl trimethyl ammonium bromide) approach by sol-gel method and a further calcination step was required [15]. Through this process, amorphous silica nanoparticles assembled from primary particles of tens of nanometers were synthesized and clustered or agglomerated [4,12]. These morphological properties of precipitated silica particles have also been reported in previous studies using acid for pH adjustment to format gel [4,14,15].

Characterization of silica nanoparticles

The elemental composition of silica nanoparticles done by AAS also showed silicon content is 46.52% However, much difference did not note in the percentages since they differ by less than 0,0001%. Silicon in RHA exists in the silica form (silicon dioxide) [13], so SiO_2 content is 99.69%. This is confirmed by EDX analysis that shows the levels of silica as 99.56%. The chemical composition of silica nanoparticles analysis by EDX was presented in Figure 3.

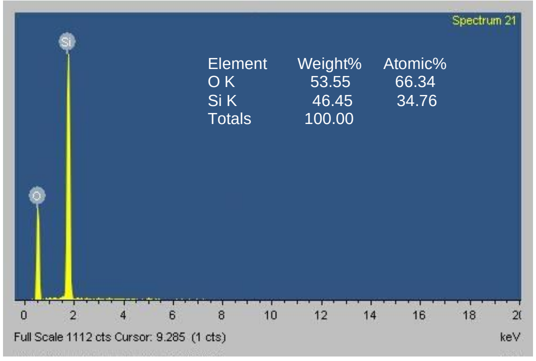

Figure 3: EDX spectrometric data of silica nanoparticles produced from RHA

As a result in Figure 3, silica nanoparticles contain only silicon and oxygen with a weight ratio of about 1:1.5. This result confirmed obtained silica nanoparticles in good stoichiometric ratio and high purity [7,10,11]. The absence of other elements, such as Ca, K, Na, Mg, Fe, Al, Mg, ... were also reported in rice straw by treatment with acid [11-13].

The FT-IR spectra measurement of synthesized silica nanoparticles did characterize the functional groups

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that are existing on the surface in the range of 4000-400 cm^{-1}, which showed in Fig. 4. Where the existence of adsorbed water and silanol groups as well as siloxane linkages can be easily recognized. Fig. 4 shows the dominant peak at 1106 cm-1 where it can be attributed to Si–O–Si asymmetric vibration which is concerning with the arrangement of dense silica organize [5,8]. The broad shoulder from 1045 - 877 cm^{-1} can be attributed to the vibration of the tetrahedral S1O4 coordination unit [12,13]. The peak 822 cm^{-1} indicates the presence of Si–O stretching vibration of the silanol group. The peak appeared at 470 cm^{-1} is related to the bending vibration of the Si–O–Si bond [5,16]. The bending vibration at 3448 and 1634 cm^{-1} was due to the H–O–H, stretching of different hydroxyl groups of adsorbed water molecules on the silica surface which reflected the high purity of silica and give adsorption characteristic of particles [8]. The band peaks are the main indicator of the silica material, which represents the successful production of silica nanoparticles from industrial waste RHA [12].

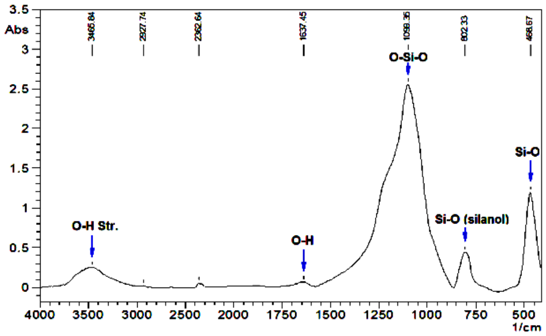

Figure 4: FT-IR spectrum of silica nanoparticles from from industrial waste RHA

The X-ray diffraction of the obtained silica nanoparticles showed in Fig. 5. The XRD result shows the presence of a broad peak at 2θ between 15 and 30° (specifically has an only single peak at 2θ ~22.1°), which confirms the presence of almost amorphous SiO_2 [3, 17-18]. The thermal treatment of SiO_2/chitosan gel generated a mixture of almost amorphous and a little crystalline SiO_2. This indicates that industrial waste RHA has great potentials as an alternative source of SiO_2, and further confirms the purity and effectiveness of the method applied herein. The result is consistent with the previous study [7,10-12], where they reported amorphous of 90.23 – 95.75% silica in RHA.

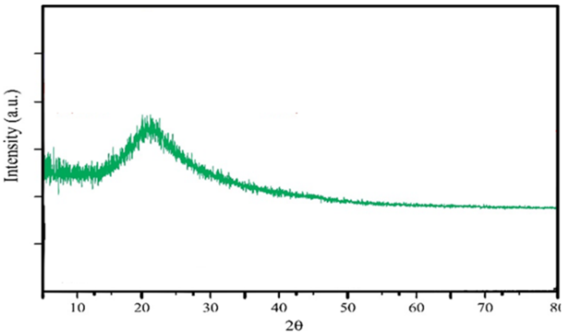

Figure 5: XRD pattern of silica nanoparicles from industrial waste RHA

Conclusion

In this study, an attempt had made to use a cheap source (industrial waste RHA) to prepare silica nanoparticles. Silica nanoparticles with small particle sizes (< 10 nm) were prepared by the pyrolysis of SiO_2/chitosan gel, which should be not only efficient but also adjustable particle size. The synthesized silica nanoparticles are almost amorphous structure and high purity (99.69%). Furthermore, this method is fairly suitable for smaller particle sizes of silica production than its previous authors. This study shows that silica nanoparticles can be potential for different application purposes where particle size is optional.

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