

Synthesis of silica nanoparticles from rice husk ash

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Abstract— Silica nanoparticles (SiO₂ NPs) were synthesized from rice husk ash (RHA) by chemical treatment and calcination. The size of SiO₂ NPs evaluated by transmission electron microscope (TEM) was of 20 - 50 nm and the size distribution of SiO₂ NPs measured by dynamic laser scattering (DLS) was of Gaussian mode. The X-ray diffraction (XRD) pattern with only one peak at 20 ~ 22° confirmed the amorphous phase of SiO₂ NPs. The Fourier transform infrared (FTIR) and energy-dispersive X-ray (EDX) spectra were also used to evaluate the functional groups and the purity of SiO₂ NPs. The SiO₂ NPs powder with high purity could be suitably produced by calcination of acid treated RHA at 700°C for 2h. The obtained SiO₂ NPs product can be potentially used for numerous purposes of application, especially as filler in paints.

Index Terms— silica nano, rice husk ash, calcination, particle size.

1 INTRODUCTION

Rice husk (RH) is a byproduct of rice milling process and RH is one of the abundant waste sources in rice growing countries such as Vietnam, Thailand, China,... It is estimated that one ton of

rice is created ~0.23 ton of RH. According to Chandrasehar et al. in India, in 1997-1998, about 26 million tons of RH were created [1]. In Vietnam, rice productivity is estimated of about 40 million tons/year, then the volume of RH waste is about 9.2 million tons/year. With silica content of about 10% in RH [2], the silica amount from RH in Vietnam is approximately one million ton/year. The presence of silica in the rice husk has been known since 1938 [1]. Commonly, RH is used as fuel with combustion energy of ~16,720 kJ/kg [3,4]. When RH is burned, it will create RH ash (RHA) with composition including: 72.1% SiO₂; 0.3% Al₂O₃; 0.43% CaO; 0.5% Na₂O; 0.72% K₂O; 0.15% MnO; 0.05% TiO₂; 0.7% MgO; 0.06% P₂O₅ and ~24.3% weight loss on ignition [3]. These components are subjected to change due to the different influenced factors such as geographic location, fertilizers, agro-chemicals,...[4]. Many studies on fabrication of silica from RH were conducted, especially silica nanoparticles (SiO₂ NPs) produced from RH in order to increase the value of agricultural waste source [2,5-9]. RHA is also an abundant source that can be used to produce SiO₂ NPs [3,4,10,11]. Silica was used for many applications such as adsorption material, carriers, fillers,... Recently, silica from RH was used for production of porous ceramic doped with nano silver to induce antimicrobial property for treatment of microorganisms in water [12]. In addition, silica and SiO₂ NPs were also used as growth promoter and elicitor for plants [9,13-17]. In the previous work [9], we studied to prepare SiO₂ NPs from RH. In this work, SiO₂ NPs was synthesized from RHA, which is also an abundant source obtained from factories using RH as burning fuel, especially in Mekong Delta region.

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2 EXPERIMENTAL.

2.1 Materials and chemicals

Raw RH was supplied by rice mill factory in the south of Vietnam. Analytical reagent-grade hydrochloric acid (HCl) was purchased from Merck, Germany. Distilled water and other chemicals were of pure grade.

2.2 Synthesis of SiO_2 NPs from RHA

SiO_2 NPs from RHA was synthesized following the procedure of Sankar et al. [11] with some modifications. Briefly, raw RH was washed with tap water to remove sand, dust, soluble substances, and other contaminants. It was then dried at 60°C in forced air oven (Yamato, DNF 410, Japan). The cleaned RH was burned in open environment to collect RHA. 50 g of RHA was stirred with 500 ml of HCl 1N at room temperature for 2 hours and allowed to stand overnight to separate the metal ions in RHA. The acid treated RHA was filtered and washed with distilled water and dried at 60°C in forced air oven. Finally, the treated RHA was transferred into porcelain cup and calcined at 700°C for 2 hours in furnace Nabertherm, Germany with a ramp rate of $\sim 20^\circ\text{C}/\text{min}$. The obtained product was SiO_2 NPs white powder (Figure 1).

2.3 Characterization of SiO_2 NPs

The particle size of SiO_2 NPs was evaluated by transmission electron microscope (TEM), model JEM1010, JEOL, Japan and the particle size distribution of SiO_2 NPs was measured by dynamic laser scattering (DLS) on a particle size analyzer, LB550, HORIBA, Japan. The X-ray diffraction (XRD) pattern was determined on D8 Advance, Bruker, Germany. Element composition of SiO_2 NPs was analyzed by energy dispersive x-ray spectrometer (EDX), Horiba 7593-H. The Fourier transform infrared (FTIR) spectrum was measured on FT-IR 8400S spectrometer (Shimadzu, Japan) using KBr pellet.

3 RESULTS AND DISCUSSION.

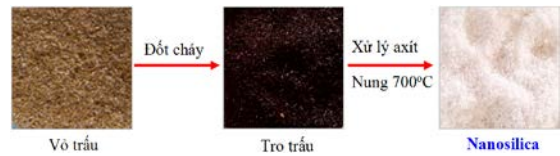


Figure 1. Brief schematic description of synthesized process of SiO_2 NPs from RHA

The brief schematic description of synthesized process of SiO_2 NPs from RHA was presented in Figure 1.

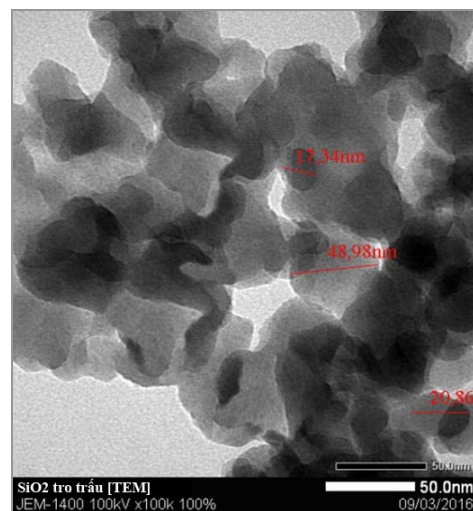


Figure 2. TEM image of SiO_2 NPs from RHA

TEM image in Figure 2 showed that the particle size of SiO_2 NPs from RHA was in the range from 20 to 50 nm. This result was consistent with the result of Sankar et al. [11], but the particle size was somewhat larger than that prepared from the RH (10-30 nm) in our previous study [9].

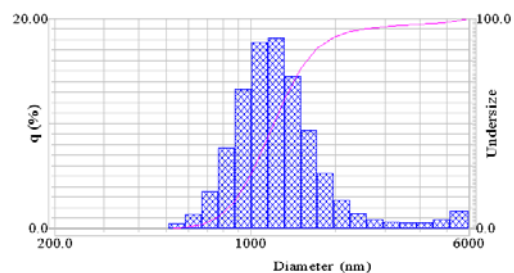


Figure 3. Particle size distribution of SiO_2 NPs from RHA measured by DLS

Result Figure 3 showed the particle size measured by DLS in the range from 800 to 1400 nm that was higher than the size determined from TEM (20-50 nm). The reason is that DLS method usually determines the dynamic diameter particle sizes of SiO₂ NPs dispersed in water [3]. Result in Figure 3 also showed that the particle size distribution of SiO₂ NPs is a bell-shaped distribution (Gaussian distribution).

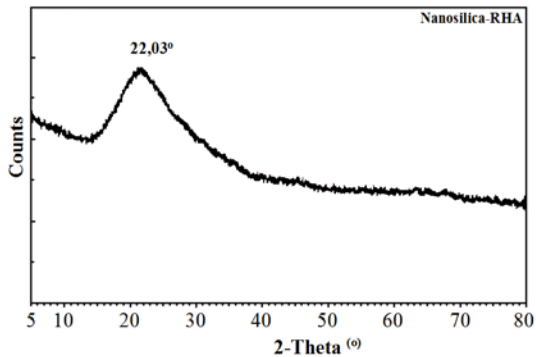


Figure 4. XRD pattern of SiO₂ NPs from RHA

XRD pattern of SiO₂ NPs in Figure 4 showed only 1 peak at $2\theta \sim 22^\circ$. The obtained result confirmed the amorphous phase of SiO₂ NPs synthesized from RHA treated with acid and calcined at 700°C for 2h [4,9].

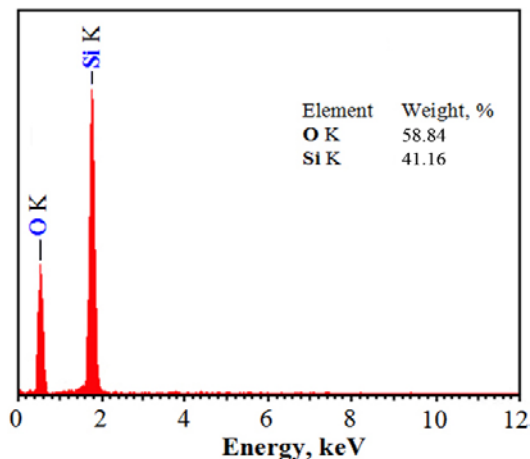


Figure 5. EDX spectrum of SiO₂ NPs from RHA

The EDX spectrum of SiO₂ NPs in Figure 5 showed 2 peaks at k_α at 1.74 and 0.53 keV corresponding to silicon (Si) and oxygen (O) with content in weight of 41.16% for silicon and 58.84% for oxygen. This result also indicated that the synthesized SiO₂ NPs was of high purity [4].

According to Le et al. [10], the composition of

Vietnam's RHA included K₂O (0.39%), Al₂O₃ (0.48%), Fe₂O₃ (0.15%), CaO (0.73 %), MgO (0.55%), Na₂O (0.12%) and SiO₂ (96.15%). Thus, the metal impurities in RHA was efficiently extracted by HCl 1N. Carmora et al. [18] reported that organic acids such as acetic acid, citric acid can be used to extract the metal ions in RH to increase the purity of SiO₂ NPs and to meet the demand for cleaner production. It can be deduced that organic acids could also be used to treat RHA.

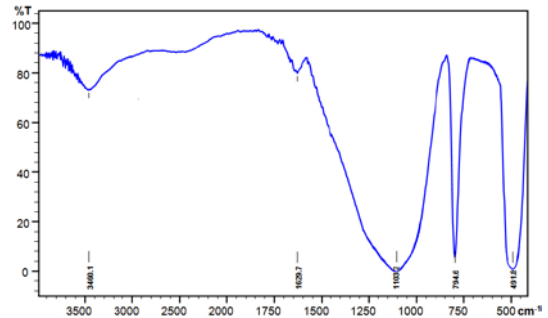


Figure 6. FTIR spectrum of SiO₂ NPs from RHA

The FTIR spectrum in Figure 6 exhibited characteristic peaks of silica framework, particularly at 1103 cm⁻¹ for the O-Si-O asymmetric stretching vibration, at 794 cm⁻¹ for the O-Si-O symmetric stretching vibration and at 491 cm⁻¹ for the O-Si-O bending vibration [4,11,19]. The broad peak at 3460 cm⁻¹ was due to the stretching vibration of surface silanol groups (Si-O-H) and physically adsorbed water [11,19,20]. In addition, the peak at 1629 cm⁻¹ was assigned to H-O-H bending vibrations of trapped water molecules in the silica matrix [19,20]. Thus, the FTIR spectrum did not show any peaks confirming the presence of other organic and inorganic materials that demonstrated high purity of the obtained SiO₂ NPs [2,11,19,20].

4 CONCLUSION.

In this study, RHA-an abundant agriculture waste was used for the synthesis of SiO₂ NPs. The SiO₂ NPs with diameter of 20 - 50 nm and high purity was successfully obtained by calcination of HCl acid treated RHA at 700°C for 2h. The synthetic process is fairly suitable for large-scale production. Thus, the synthesized SiO₂ NPs, a value-added product can be potentially used for different applications, especially as filler in paints

and helps to diminish the concerns of RHA disposal in environment as well.

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Nghiên cứu tổng hợp nanosilica từ tro trấu

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Tóm tắt— Nanosilica được chế tạo từ tro trấu bằng phương pháp xử axit và nung. Kết quả cho thấy kích thước hạt của nanosilica xác định bằng chụp ảnh kính hiển vi điện tử truyền qua (TEM) trong khoảng 20 - 50 nm. Phân bố kích thước hạt nanosilica theo kiểu hình chuông (Gaussian) được đo bằng phương pháp tán xạ laser (DLS). Phổ hồng ngoại (FTIR) và phổ tán sắc năng lượng tia X (EDX) cũng được sử dụng để đánh giá nhóm chức năng và độ tinh khiết của vật liệu nanosilica. Kết quả cũng cho thấy vật liệu nanosilica có thể được chế tạo một cách thuận lợi bằng phương pháp nung tro trấu đã được xử lý với axit ở nhiệt độ 700°C trong thời gian 2 giờ. Sản phẩm nanosilica có tiềm năng đáp ứng nhu cầu ứng dụng trong nhiều lĩnh vực, đặc biệt là làm chất độn pha sơn.

Từ khóa— Silica nano, tro trấu, thiêu kết, kích thước hạt.