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Characteristics of Silica Nanoparticles from Rice Husk as Influenced by Surface Modification with Used Solvent Containing Silane

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Highlights:

- Modification of silica nanoparticle surface from rice husk using a silane coupling agent (bis-(3-triethoxysilylpropyl) tetrasulfane (TESPT)) could improve silica nanoparticle performance.
- The resulted filtrate containing silane TESPT could be reused as solvent in the next process of silica nanoparticle surface modification.
- The used solvent still effectively modified the silica nanoparticle surface as indicated by almost the same characteristics of the silica nanoparticles modified by the used solvent as those modified by fresh solvent.
- Modification of silica nanoparticles using One Step Modification (OSM) and Two Step Modification (TSM) was effective in increasing the performance of the silica.

Abstract. Silica extracted from rice husk (silica nanoparticles, Si-NP RHA) has great potential for industrial use, particularly as filler in the rubber industry. However, silica is poorly dispersed in the matrix and needs to be modified by a silane linking agent (bis-(3-triethoxysilylpropyl) tetrasulfane (TESPT)) to improve its mixing properties. As a result, a large amount of used solvent containing silane TESPT is produced. This study aimed to evaluate the surface modification of silica nanoparticles from rice husk employing this used solvent and to characterize the particles' physical properties. Silica nanoparticles were extracted from rice husk using a sol-gel method. FTIR spectography demonstrated that the TESPT on fresh solvent and the used solvent were successfully grafted onto the surface of Si-NP RHA. Si-NP RHA modified by Two Step Modification (TSM) employing used solvent had strong absorption peaks at wave numbers of 2927.94 cm^{-1} and 1446.61 cm^{-1}, which are associated with vibration of the -CH_2 group and deforming vibration of the -C-H group in TESPT compounds. Likewise, Si-NP RHA modified with One Step Modification (OSM), either using fresh solvent or the used solvent, exhibited absorption peaks at wave numbers 2935.66 cm^{-1} and 1404.18 cm^{-1}. The result showed that the used solvent still effectively modified the silica nanoparticle surface.

Keywords: *reuse; rice husk; silane coupling agent; silica nanoparticles; surface modification.*

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1 Introduction

Silica (SiO_2) is a material with excellent physical and chemical properties, particularly due to its unique advantages in the form of the surface/interface effect, good stability, and heat resistance at high temperature [1]. Thus, it has a lot of benefits in the development of industrial products such as rubber, medical equipment, plastics, polymers, paints, paper, pesticides, catalysts, film substrate, insulators, composites, and biomaterials [1,2]. Rubber compound industries use silica as an important filler to increase the performance and compatibility of their products. Previous studies have shown that silica can be extracted from rice husk, which is a renewable, biodegradable, cheap and abundant rice milling byproduct. Besides, silica from rice husk is amorphous, ultra-fine, and very reactive. Rice husk ash contains approximately 80% to 90% SiO_2 [3]. Casnan, *et al*. (2019) reported that scaled-up production using pyrolysis could produce rice husk silica with 63.99% to 82.74% purity [4]. On the other hand, the sol-gel method using a technical grade solvent developed by Setyawan, *et al*. (2019) yielded 62.83% of rice husk silica nanoparticles with 86.17% purity [5].

The surface structure of silica nanoparticles is covered with hydroxyl group (-OH), producing a strongly hydrophilic surface. According to Kang e*t al*., the hydrophilic surface characteristic of silica nanoparticles makes it difficult to disperse them well and they become unstable in organic solutions or in solid materials [2]. Therefore, a surface modification process is required to improve this characteristic of silica nanoparticles to enable wider application. A number of surface modification methods using a silane coupling agent have been reported in previous studies [1,2,6-11]. Alkadasi, *et al*. found that successful filling of a silane coupling agent on the silica surface structure improved its crosslinking bond characteristic during curing [6].

Modification of the silica surface with a silane coupling agent commonly uses excessive organic solution to accelerate hydrolysis of alkoxy groups from the silane coupling agent so that silanol groups (-SiOOH) are produced [6]. Li, *et al*. modified the silica structure using an ethanol solution containing bis(3-triethoxysilylpropyl) tetrasulfide (TESPT) as coupling agent with a mass ratio of 1:10 (silica:solvent) [12]. More recent studies developed different surface modification methods involving the use of acetone solution containing KH-560 as silane coupling agent at a mass ratio of 1:5 (SiO_2 nanoparticle:acetone) [1] or a toluene solution containing dimethyldichlorosilane (DMDCS) as coupling agent at a ratio of 1:60 (silica mass:toluene volume) [10]. The process of silica surface modification using a silane coupling agent in an organic solution produces a large amount of filtrate as waste. The filtrate is a solvent that still contains silane hydrosylates and has great potential to be reused in the process of silica surface modification, which may significantly reduce the production cost.

This has not yet been studied elsewhere. Thus, the aim of this study was to evaluate the characteristics of silica nanoparticles from rice husk, modified employing used solvent containing silane bis-(3-triethoxysilylpropyl) tetrasulfane solution.

2 Experimental Method

2.1 Materials

Rice husk was obtained from rice milling units in Karawang, Indonesia. Commercial silica produced by Solvay Fine Chemical Additives Qingdao Co., Ltd., silane coupling agent bis-(3-triethoxysilylpropyl) tetrasulfane (TESPT), ethanol 96%, acetate acid used for surface modification were of technical grade. Chemicals for silica nanoparticle extraction (sodium hydroxide and hydrochloric acid) were also of technical grade and were purchased from PT Brataco. All chemicals were used without further purification.

2.2 Extraction of Silica Nanoparticles from Rice Husk

Silica nanoparticles were extracted from the rice husk (Si-NP RHA) using the sol-gel method according to Setyawan, *et al*. with some modifications [5]. Seventy-five kilogram of rice husk ash (RHA) was mixed with NaOH 1 N solution at a mass ratio of 1:5. The mixture was heated at 115 °C for 3 h with constant stirring. The solution was filtered using a filter cloth. The filtrate was allowed to cool at room temperature and a large amount of HCl (1 N) was added up to pH 7. The silica gels formed were aged for 24 h and then washed with water four times. The gels were dried at 70 °C for 24 h to produce xerogels. These processes were carried out in a processing line in the Rice Quality and Cereals Postharvest Laboratory at the Indonesian Center for Agricultural Postharvest Research and Development in Karawang, West Java. The silica (Si-NP RHA) produced from the extraction process was further ground and sieved into two different sizes, i.e. 200 mesh (fine powder) and 100 mesh (coarse powder).

2.3 Surface Modification of Silica Nanoparticles

Silica surface modification was conducted using one step modification (OSM) and two step modification (TSM) according to Li, *et al*. with some modifications [9]. In the OSM technique, TESPT hydrolysates are dissolved in ethanol to give a concentration of 8%. Silica was added into the TESPT solution at a mass ratio of 1:4. The mixture was mixed using a magnetic stirrer at a speed of 350 rpm for 30 minutes at room temperature. In the TSM technique, TESPT is hydrolized in ethanol containing acetic acid. The acidic ethanol solution was prepared by adding acetic acid (around 1%) into ethanol to give a final pH of 4.5. The TESPT

was gradually added into acidic ethanol to give a concentration of 8%. The mixture was stirred for 10 hours for complete hydrolysis of the TESPT. Silica nanoparticles were added into the TESPT solution at a mass ratio of 1:10 and mixed with a magnetic stirrer at a speed of 350 rpm for 24 h at room temperature. The modified silica nanoparticles were then separated from the solution by filtration, air-dried for 12 hours and oven-dried at 100 °C for 5 hours. The filtrates (the used solvent containing residual TESPT) resulted from both the OSM and the TSM technique were reused for the next silica nanoparticle surface modification. Each treatment was repeated twice.

2.4 Characterization of Silica Nanoparticles

Characterization was done for both unmodified and modified silica, including SiO_2 purity by X-ray fluorescence spectrometry (XRF, Rigaku primus ZSX IV), crystallinity by X-ray diffractometer (XRD Bruker D8 Advance), functional groups by Fourrier transform infrared spectroscopy (FTIR, Bruker-German), particle size measurement (Zeta-sizer Nano-ZS, Malvern Instruments Ltd., Malvern, UK), specific surface area calculation by Brunauer-Emmett-Teller/BET method (Quadrasorb SI, Quantachrome Instruments Co., USA) and microstructure characterization by scanning electron microscopy (SEM Zeiss EVO MA10). The chemical composition of Si-NP RHA was measured via X-ray fluorescence spectrometry. The functional groups were analyzed by mixing spectral-grade KBr powder at a weight ratio of 1:100 mg with the different silica powders in an agate mortar. The mean diameter and standard deviation of the silica nanoparticles were determined by dynamic light scattering using a Zeta-sizer Nano-ZS, Malvern Instruments Ltd., Malvern, UK [2]. The specific surface area was determined using the Brunauer-Emmett-Teller (BET) method. Prior to measurement, the samples were degassed at 523.15 K for 7 hours. The infrared (IR) absorption spectra of the silica composite pellets were obtained by FTIR spectroscopy (FTIR Shimadzu) over a wave number range from 4000 to 400 cm^{-1} [13]. The X-ray diffraction patterns were obtained using CuKα as the radiation source (λ = 1.54060Å) operated under a constant current of 35.0 mA at 40.0 kV with a diffraction angle (2θ) scan range from 5.000° to 80.009° at a speed of 5.0°/min [14]. The microstructure of the silica nanoparticles was examined using a scanning electron microscope. The surface of the samples was coated with gold before imaging and observed with an accelerating voltage of 16.00 kV and a working distance (WD) of 6.5 to 7.0 mm.

3 Results and Discussion

The silica nanoparticles (Si-NP RHA) extracted from the rice husk ash using a sol-gel method had different characteristics from the commercial silica powder. The Si-NP RHA had a slightly higher silica (SiO_2) purity (90.87%) than that of

the commercial silica (88.31%). The average particle size of the Si-NP RHA was larger than that of the commercial silica, i.e. 847.0 nm and 667.8 nm, respectively. The specific surface area (BET) of the Si-NP RHA (103.17 m^2/g) was smaller than that of the commercial silica (135.12 m^2/g), which is related to the larger average particle size of the Si-NP RHA. This may be associated with the large amount of hydroxyl groups (-OH) in the Si-NP RHA, which tend to attract each other and form clusters with larger size. According to Alkadasi, *et al.*, the larger the particle size, the smaller the specific surface area [6]. The Si-NP RHA was more amorphous (48.90%) than the commercial silica (46.4%), which could explain the tendency of the Si-NP RHA to agglomerate and form larger clusters as compared to the commercial silica. Surface modification was carried out on the Si-NP RHA to improve the surface structure in order to increase its compatibility during the mixing process with the rubber matrix. Both OSM and TSM changed the physicochemical characteristics of the Si-NP RHA.

3.1 Specific Surface Area

The specific surface area is an important parameter, determining the functional-filling properties of a material. Surface modification altered the specific surface area (BET) of the Si-NP RHA, both using OSM and TSM (Figure 1). Overall, surface modification increased the BET surface area of the Si-NP RHA with a smaller particle size (100 mesh). The surface modification of the Si-NP RHA with a small particle size also gave a larger BET surface area than those with a larger particle size (200 mesh). In the Si-NP RHA with a particle size of 200 mesh, surface modification resulted only in slight changes in the BET surface area. In general, the use of used solvent provided the Si-NP RHA with a smaller BET surface area than the use of fresh solvent. Nevertheless, the used solvent produced a larger BET surface area than without modification treatment. This means that used solvent can potentially be reused in surface modification. Silica surface modification using a silane coupling agent can increase the specific surface area and the capability to be well-dispersed and well-distributed in a composite [1].

The reaction time in the Si-NP RHA modification process by OSM was also evaluated. Increasing the reaction time from 1 h to 2 h did not significantly increase the specific surface area of the Si-NP RHA compared to the unmodified silica. However, there is still potential for the used solvent to increase the specific surface area by increasing the reaction time to 2 hours. This is in line with the FTIR analysis results (Figure 2), which showed strong absorption during the TSM treatment for 24 hours as a result of vibration of the $-CH_2$ group from the TESPT compounds. Meanwhile, OSM treatment for 30 minutes had a weak peak compared to TSM treatment. The effectiveness of the silane grafting process on the surface of the oxide compounds is greatly influenced by the reaction

temperature, reaction time, and the weight ratio of silane to oxide compounds [15].

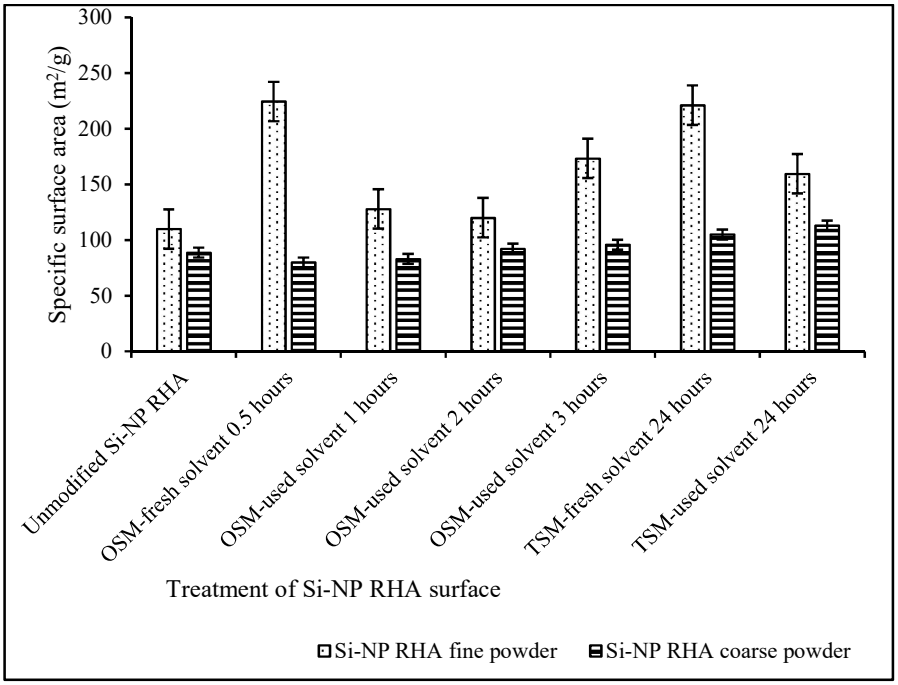

Figure 1 Specific surface area of the Si-NP RHA before and after modification with TESPT.

3.2 Functional Groups

The structure changes in the Si-NPs as influenced by surface modification were characterized using FTIR spectroscopy. All samples, the commercial silica, the unmodified Si-NP RHA, the Si-NP RHA modified with fresh solvent and the Si-NP RHA modified with used solvent, had typical silica peaks, i.e. stretching vibration of Si-OH and Si-O-Si around 3450-3200 cm^{-1} and 1000-1100 cm^{-1}, respectively. Furthermore, all samples also had a specific peak profile attributed to bending vibration modes of the hydroxyl groups (-OH) of physical adsorbed water molecules and silanol groups at wave numbers around 1600-1650 cm^{-1}. The commercial silica powder had a wide absorption peak attributed to silanol groups with Si-OH stretching vibration at wave numbers around 3415.93-3383.14 cm^{-1} and Si-O-Si stretching vibration from siloxane groups at wave number 1099.43 cm^{-1}. Similarly, the Si-NP RHA had a widened absorption peak due to vibration of Si-OH (wave length area 3427.51 to 3234.62 cm^{-1}) and Si-O-Si stretching

vibration from siloxane groups at approximately 1100 cm^{-1}. The silica had an absorption peak caused by Si-O-Si stretching vibration at around 1000-1150 cm^{-1} [11,13] and Si-OH stretching vibration from the silanol group at 3400 cm^{-1} [9]; 3430 cm^{-1} [11]; and 3434.33 cm^{-1} [16].

The successful grafting of the surface of the TESPT Si-NP was identified by the appearance of peaks at wave numbers around 2850-2930 cm^{-1} and 1450-1350 cm^{-1} as a result of methylene group (-CH_2-) vibration and deforming vibration of -C-H from the TESPT compounds, respectively [9,13,17]. The presence of peaks with strong absorption was observed at 2933.73 cm^{-1} for TSM and peaks with weak absorption at 2926.01 cm^{-1} for OSM (Figure 2), indicating successful grafting of TESPT onto Si-NP particles. The presence of these methylene vibrations were not found in the sample without surface modification treatment.

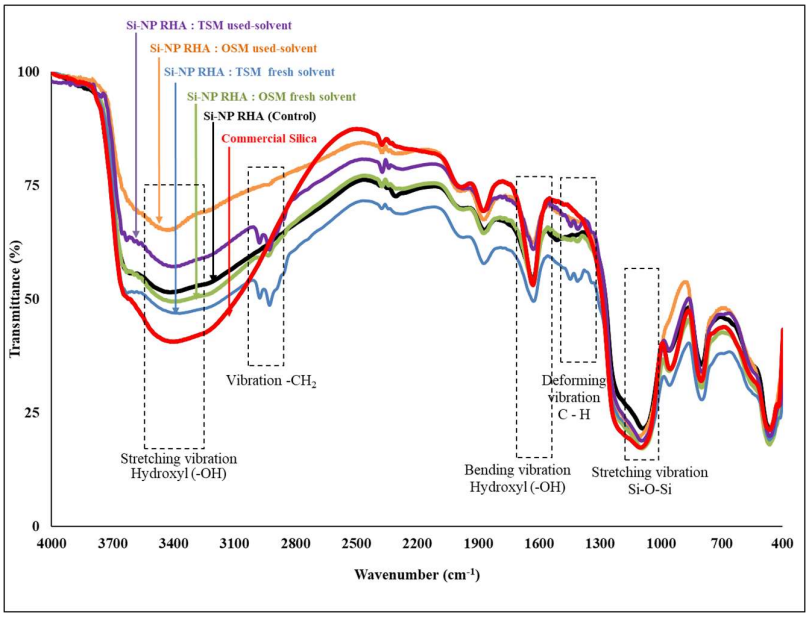

Figure 2 FT-IR spectra of the Si-NP RHA before and after modification with TESPT.

Figure 2 shows that the FTIR spectrum of the Si-NP modified by TSM using used solvent had a strong absorption peak at wave number 2927.94 cm^{-1} and 1446.61 cm^{-1} associated with -CH_2 group vibration and deforming vibration of the -C-H group from the TESPT compounds. Two other samples, the Si-NP modified with OSM, either using fresh or used solvent, exhibited peaks around wave numbers

2935.66 cm^{-1} and 1404.18 cm^{-1}. Although the adsorption peaks were weak, these demonstrated that TESPT was successfully grafted onto the Si-NP surface.

3.3 Crystalline and Amorphous Characteristics

Xiao, *et al.* mention that silica modified using silane coupling agent TESPT is amorphous [11]. Figure 3 shows the XRD patterns of the commercial silica, the pure Si-NP RHA, the Si-NP RHA modified with fresh solvent and with used solvent. This figure shows that the process of Si-NP RHA surface modification using fresh solvent and used solvent had no significant influence on the diffractogram patterns. All silica samples had a typical dispersion peak in the 2-theta area of around 22° to 23°. This 2-theta area is the glass state characteristic of amorphous silica [18,17]. This indicates that the surface modification did not change the structure of the Si-NP RHA. The amorphous percentage of the unmodified Si-NP RHA modified by OSM-fresh solvent, TSM/fresh solvent, OSM/used solvent and TSM/used solvent were 48.5%, 44.4%, 46.9%, 50.1% and 44.5%, respectively. The Si-NP RHA modified by used solvent had amorphous characteristics that were not significantly different from those modified by fresh solvent. Thus, used solvent can potentially be reused in surface modification.

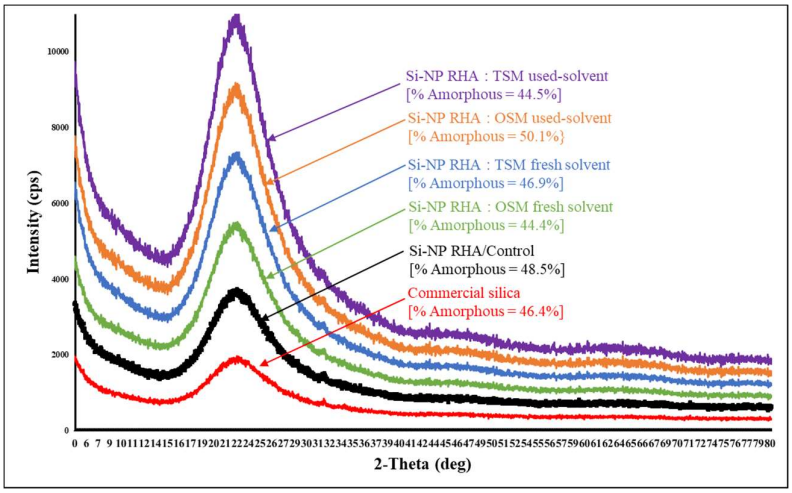

Figure 3 XRD pattern curves of the Si-NP RHA: unmodified; modified with fresh solvent; modified with used solvent containing TESPT.

3.4 Surface Morphology Results

The surface morphology was evaluated using SEM. Figure 4 shows that all the samples, i.e. the commercial silica, the unmodified and modified Si-NP RHA, had a similar nano-structure. Si-NP RHA (Figure 4b) shows more agglomerated

particles forming aggregates than the commercial silica (Figure 4a). Figure 4c shows the morphological structure of the modified Si-NP RHA with fewer aggregates than the unmodified samples in Figure 4b. This demonstrates that the modification process of the Si-NP RHA surface using TESPT was able to prevent silica particle agglomeration, resulting in smaller particle sizes. This is associated with increased potential energy on the modified silica surface, leading to resistance to the agglomeration process [1].

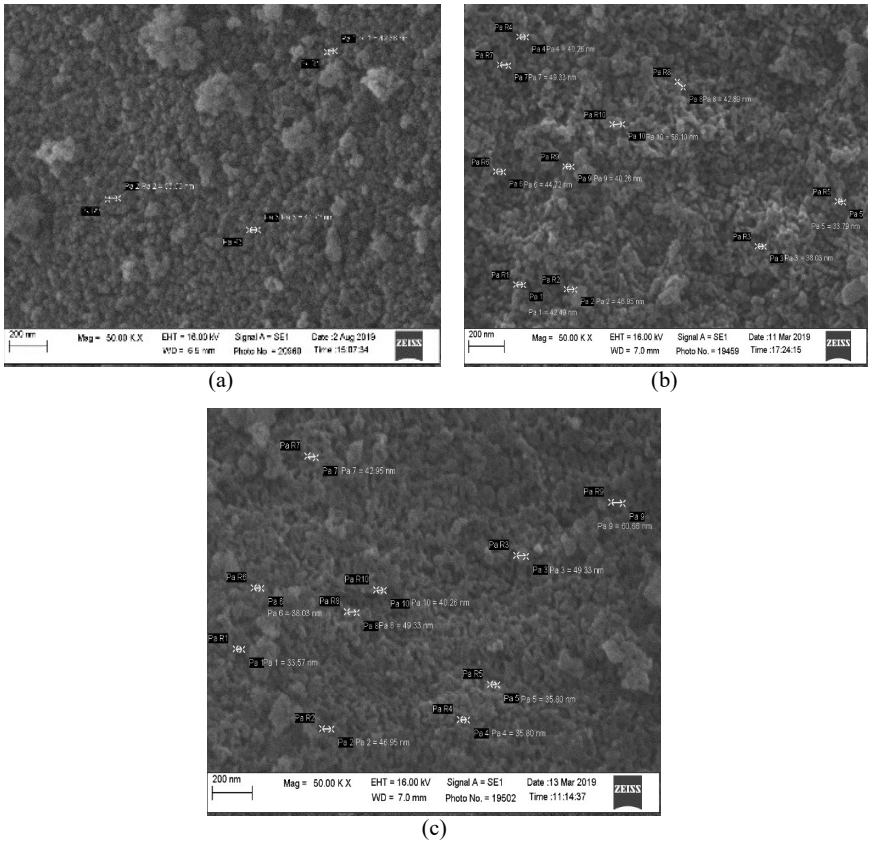

Figure 4 SEM images of (a) the commercial silica (b) the Si-NP RHA (unmodified); (c) the Si-NP RHA (surface modified with TESPT) at a magnification of 50,000x.

4 Conclusion

Used solvent containing silane bis-(3-triethoxysilylpropyl) tetrasulfane (TESPT) was successfully utilized to modify the surface of silica nanoparticles from rice

husk (Si-NP RHA). This was shown by the FTIR spectra, which indicated grafting of TESPT onto the surface of the modified Si-NP RHA. The use of used solvent provided Si-NP RHA with a larger BET surface area than without modification treatment, indicating successful surface modification. The characteristics of the Si-NP RHA modified by used solvent can be improved by increasing the modification processing time. The morphological structure on the surface of the Si-NP RHA modified using TESPT was able to prevent silica particle agglomeration, resulting in smaller particle sizes. These findings provide useful information for high-efficiency manufacturing of modified Si-NP RHA.

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