A facile approach to synthesis of silica nanoparticles from silica sand and their application as superhydrophobic material

A. Ismaïa, L. N. M. Z. Saputri², A. A. Dwiamoko³, B. H. Susanto⁴ and M. Nasikin⁵

¹Department of Chemical Engineering, Universitas Indonesia, Depok, Depok, Indonesia; ²Department of Chemistry, Universitas Indonesia, Depok, Depok, Indonesia; ³Research Center of Chemistry, Indonesian Institute of Sciences, Serpong, Indonesia

ABSTRACT

We present a facile method to produce silica nanoparticles as a superhydrophobic material which has been successfully synthesized by mechanical milling and the sol–gel method. The powder obtained was characterized using scanning electronic microscopy, X-Ray Diffraction, particle size distribution, and zeta potential. The effects of alcohol solvents on synthesis, such as on particle size, particle size distribution, and zeta potential, were examined thoroughly. To evaluate the surface modification of silica nanoparticles from hydrophilic to hydrophobic properties, IR spectra was applied. Surface modification was conducted prior to the evaluation of the superhydrophobic properties of silica nanoparticles on the glass substrate. In this study, silica nanoparticles in the ethanol solvent achieved optimum results with a particle size of 170.3 ± 14.3 nm and the highest zeta potential of −50.4 ± 0.3 mV, which is the best superhydrophobic effect on the glass substrate. In addition, the superhydrophobic effect of the silica nanoparticles was also applied to the bitumen, as both coating and mixing with the water contact angle was increased to 149.2° and 148.1° compared to the bitumen without silica nanoparticles. Due to their simplicity and low-cost, modified silica nanoparticles show great potential for industrial applications as superhydrophobic material on the bitumen.

1. Introduction

Superhydrophobic surfaces have grown greater an interest to researchers due to their wide practical applications as in self-cleaning and anti-icing applications [1,2]. A material surface is said to have a superhydrophobic effect when it has a contact angle with water larger than 150° [3]. Its characteristics are the increased contact angle and formed air pockets in the interface due to rough morphology and low surface energy [4]. Superhydrophobic surfaces have been fabricated from various materials like polymers, metal oxide, and nanoparticles [5–9]. However, nanoparticles, especially silica particles, offer more advantages than other materials because of their earth-abundance, ease of synthesis, and their stability [10]. Despite its lower costs, agglomeration issues [11] prevent the scaling-up of silica use for industrial applications. Therefore, studies on the synthesis of silica nanoparticles with simple and low-cost methods have been conducted to obtain more promising properties.

Silica nanoparticles have hydrophilic properties because of their attached hydroxyl group on the surface. To transform the properties on the silica particles’ surfaces from hydrophilic to hydrophobic, fluorinated hydrocarbons are used to modify the hydroxyl group [12,13]. However, due to cost and environment issues, modification of the silica particles with stearic acid is more favorable than with fluorinated hydrocarbons [14]. Silica nanoparticles are synthesized by various methods such as ball milling, hydrothermal, chemical vapor deposition, microemulsion, and sol–gel [15–20]. For the purpose of obtaining silica particles with uniform size, high purity, ease to control, and scalability, the sol–gel process is the most popular. In this method, the reaction is controlled under either an acid or alkaline condition, in which case metal alkoxides, such as TEOS or inorganic salts like sodium silicate, are used as precursors [21]. However, because TEOS is a high-cost material, sodium silicate solution, as a precursor, is more preferable. Several researchers have reported the synthesis of silica particles using fly ash, bentonite, rice husk, bagasse ash, and silica sand by the sol–gel process [22–25].

As mentioned above, sol–gel is a synthesis method that is suitable for industrial manufacturing due to its simplicity, homogeneity, and refined result. The importance of the sol–gel process in the formation of the silica particle structure has been studied by Zulfiqar et al. [26], who synthesized silica nanoparticles from a sodium silicate solution using sol–gel under alkaline conditions to prevent agglomeration. The results showed that the sizes of the silica nanoparticles could

CONTACT M. Nasikin mnasikin@che.ui.ac.id Department of Chemical Engineering, Depok 16424 Indonesia

© 2021 The Author(s). Published by Informa UK Limited, trading as Taylor & Francis Group on behalf of The Korean Ceramic Society and The Ceramic Society of Japan. This is an Open Access article distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/4.0/), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.
be decreased by increasing the pH in the reaction system. Another effect of pH has been observed by Isobe et al. [27], who synthesized porous silica particles from a spray-dried sodium silicate solution. The results reported that the formation of micropores are influenced by the pH of the sodium silicate solution. Rao et al. [28] demonstrated that the size and dispersity of silica nanoparticles are affected by alcohol solvents. The smallest size of silica particles was obtained in methanol solutions, while the particle size increased with the lengthening of the alcohol chain. In addition to the pH and solvent, Ismail et al. [22] reported that the silicon content in the sodium silicate solution leads toward production of nuclei due to enhanced solubility of intermediate species during the reaction of silica nanoparticles. The study showed that to increase the silicon content in the sodium silicate solution, the size of silica powder from silica sand should be decreased by mechanical milling.

Silica sand is abundant in Indonesia with high-purity silica content and plays an important role for various industries. However, there have been few studies regarding the use of silica sand as a raw material to prepare the sodium silicate solution as a precursor to synthesize silica nanoparticles. The conventional synthesis of silica nanoparticles from silica sand is conducted by alkali fusion [29] and mechanical milling [30]. Munasir et al [29], obtained amorphous silica nanoparticles with the particle size of about 60 nm by going the alkali fusion route using NaOH at 500 °C. The synthesis of silica nanoparticles using the mechanical milling method was observed by Wahyudi et al. [30]. High-grade results were achieved by using the planetary ball mill for 30 hours with an average particle size of 80 nm. Although the method generates a very fine particle size, it produces particle agglomeration which can affect the performance of hydrophobic properties. In fact, mechanical milling is a synthesis method that offers simplicity, low cost, and low chemical waste [30]. However, another method is needed to successfully achieve silica nanoparticles with controlled particle size and shape.

In this study, we introduce the preparation of silica nanoparticles using a combination method that involves a simple, scalable, and stable process by mechanical milling and sol–gel. Instead of using alkaline medium to prevent agglomeration, we used acidic medium which is more soluble in alcohol solvents. In addition, we carried out purification to remove any residual impurities. The particle size and zeta potential were investigated with various alcohols. We also fabricated the superhydrophobic silica nanoparticles according to modification of the surface by stearic acid [14]. Finally, the superhydrophobic effect of the silica nanoparticles was applied to the bitumen as both coating and mixing.

2. Materials and methods

2.1. Materials

The raw material used to produce silica nanoparticles was supplied from silica sand on Belitung Island, Indonesia. According to X-ray fluorescence (XRF) analysis, the SiO₂ concentration of silica sand is about 99.42%. All the chemicals used were nitric acid, hydrochloric acid, sodium hydroxide, methanol, ethanol, and 2-propanol, purchased from Merck. Distilled water was used throughout the entire process.

2.2. Methods

2.2.1. Preparation of sodium silicate (aqueous) solution (SSS)

Silica sand was milled by high-energy milling in order to reduce the size of silica sand to form a silica powder of 325 mesh. The ball-milled silica powder was diluted with 2 M NaOH at 90° for 2 hours and then filtered to get the sodium silicate solution (SSS).

2.2.2. Synthesis of silica nanoparticles

A mixture was prepared with 50 mL of SSS and 20 mL of ethanol. The suspension was neutralized with 5 M HNO₃ to reach a pH of about 7. The solution was stirred for 2 hours then sonicated for 30 minutes. For heat dissipation, ultrasonic irradiation was carried out in an iced bath environment. After settling down, the white transparent gel was separated from the solution by filtration. The white transparent gel was washed by distilled water and centrifuged for 10 minutes in 5 circles at 5000 rpm at room temperature. To remove the sodium and other impurities, the white transparent gel was washed again with 8 M HCl solution and sonicated for 30 minutes. Then the solution was washed with distilled water by centrifugation at 5000 rpm until pH 7 was reached again. The white powder of silica nanoparticles was obtained after drying for 48 hours. Synthesis was also conducted with methanol and propanol.

2.2.3. Thin film of modified silica superhydrophobic

Silica nanoparticles were mixed with stearic acid (1:5 w/w) in 25 mL of ethanol based on a previous study [31]. The mixture was subjected to stirring and heating at 60 °C for 2 hours. Then the glass substrate got into the solution for 5 hours until silica gel formed. The film was air-dried at 100 °C in air using a hot plate.

2.2.4. Preparation of superhydrophobic bitumen

The bitumen was prepared by two types of applications i.e. coating and mixing. For the coating process, first the glass substrate was coated with bitumen, then with superhydrophobic nano-silica. The bitumen on the glass substrate was dipped into the solution for 5 hours until silica gel formed. The film was dried at
100 °C in the air using a hot plate. The mixing bitumen was prepared by adding formulated nano-bitumen i.e. 1% of superhydrophobic nano-silica by weight of bitumen and mixing them for 1 hour at a temperature of 100 °C. The glass substrate was washed several times with alcohol and deionized water and dried in an oven. Then, the glass substrate was immersed in the mixing bitumen suspension and dried several days at room temperature.

2.3. Characterization

Compositional analysis of silica sand was performed with X-ray fluorescence (S2 Ranger). The silica nanoparticles were purified by centrifugation (Hanil Fleta 5) for 5 runs at 5000 rpm at room temperature. X-ray diffraction (XRD) of silica nanoparticles was performed for the phase analysis (Broker D8 Advance, CuKα, λ = 1.54059, scan step size 0.02173, time per step 23.970). The peak was compared to the JCPDS 29–0085 of the International Center for Diffraction Data to determine the crystalline structures. Morphological examination of silica nanoparticles was performed by using scanning electron microscopy (FEI Quanta 650). Particle size distribution was obtained by analyzing the SEM images using the Image J software. The information on the super hydrophobicity and the degree of modification of silica nanoparticles was obtained by measuring the contact angle of the droplet at 40 μL the silica thin film areas of each sample using a contact angle on the Image J software at room temperature.

3. Results and Discussion

In this study, we used silica sand as a source of sodium silicate solution (eq. 1) and controlled the formation of silica nanoparticles with HNO₃ using the sol–gel method. The formation of silica nanoparticles was based on the reaction of the sodium silicate solution with HNO₃ as shown by eq. 2. and the white fine powder of silica nanoparticles was obtained after drying for 48 hours (eq. 3). Previously, silica sand was milled for 30 minutes by using high-energy milling to obtain silica powder with a particle size of approximately 325 mesh.

\[
\text{SiO}_2(\text{s}) + 2\text{NaOH}_{(aq)} \rightarrow \text{Na}_2\text{SiO}_3(\text{aq}) + \text{H}_2\text{O}_{(l)} \quad (1)
\]

\[
\text{Na}_2\text{SiO}_3(\text{aq}) + 2\text{HNO}_3(\text{aq}) + \text{H}_2\text{O}_{(l)} \rightarrow 2\text{NaNO}_3 + \text{Si(OH)}_4(\text{aq}) \quad (2)
\]

\[
\text{Si(OH)}_4(\text{aq}) \rightarrow \text{SiO}_2(\text{s}) + 2\text{H}_2\text{O}_{(l)} \quad (3)
\]

Figure 1(a–c) shows SEM images of silica nanoparticles in varying alcohols, i.e. methanol, ethanol, and n-propanol, respectively. The microstructure of silica nanoparticles shows non-agglomerated, spherical-shaped, and uniform-sized particles. It can be supposed from the result that the particle size grew with the increasing chain length of the alcohol. The particle size of the silica nanoparticles is shown in Figure 1d. The silica nanoparticles produced in methanol had a size of 149.1 ± 10.7 nm, which increased to 170.3 ± 14.3 nm and to 198.6 ± 19.5 nm after varying the solvent to ethanol and 2-propanol, respectively. Figure 1d shows that the silica nanoparticles, synthesized in ethanol solvent, had the highest zeta potential of about −50.4 ± 0.3 mV, followed by those synthesized in the methanol (−72.2 ± 1.6 mV) and 2-propanol (−67.5 ± 0.2 mV). These results indicated that the silica nanoparticles in ethanol tended to resist agglomeration, which was electrically stabilized as can be seen in

Figure 2 graphically shows the change in particle size distribution with variations of alcohol solvents. It can be observed that not only the particle size, but also the particle size distribution, increased continuously with the increasing chain length of the alcohol. However, although the particle size distribution became broader due to the effect of alcohol chain, the monodisperse and uniform-sized particles were obtained in the ethanol (Figure 2b). This result also aligns with the previous reports, indicating that ethanol plays a major role in the impact of silica nanoparticles on monodispersity and narrow size distribution [26,28]. Interestingly, the particle size distribution of the silica nanoparticles synthesized in the methanol (Figure 2a) revealed poor uniformity. By contrast, in 2-propanol (Figure 2c), the particle size distribution of silica nanoparticles was observed to have the uniformity of particle population, much like that of the silica nanoparticles synthesized in the ethanol but with a larger particle size. From the observation, it can be concluded that particle size distribution was related to solvent polarity which affected the nucleation and particle growth of the silica particles. Methanol is the most polar alcohol solvent which can increase the solubility of sodium silicate and thus produce a high concentration of very small silica nuclei that might be growing independently, strong in polydispersity [32,33]. Different from methanol, ethanol and 2-propanol generated a lower level of supersaturation and concentration gradients during particle growth, giving rise to monodispersity and uniformity of silica particles.

Using the synthesized silica nanoparticles in various alcohol solvents, superhydrophobic silica nanoparticles were fabricated. To further evaluate the superhydrophobic properties of silica nanoparticles, surface modification was conducted by mixing the silica nanoparticles with stearic acid. Figure 3 shows the FTIR spectra of modified silica nanoparticles. The peaks appearing at 1,099 cm⁻¹ confirmed the presence of Si–O–Si bonds. As shown in Figure 3a, the peaks at 1,466.93 cm⁻¹ corresponded to the asymmetric Si–C
bond, which did not appear in silica nanoparticles (Figure 3b). In addition, the asymmetric and symmetric stretching vibrations of C–H were identified at 2,922 cm\(^{-1}\) and 2,851.88 cm\(^{-1}\), respectively. The presence of C–H bonds confirmed the grafting of methyl groups to silica particles, and the presence of C = O at 1,705.15 cm\(^{-1}\) could be attributed to stearic acid that was attached to the silica particles. The values of these silica nanoparticles in FTIR spectra were in good agreement with the previous study [34]. Therefore, it was concluded from the results that the modification at the surface of silica nanoparticles has already occurred by the replacement of – OH moieties with – Si–(CH\(_3\))\(_3\), identified by the peak at 3,750 cm\(^{-1}\) which disappeared. The formation of silica nanoparticles (Figure 4) was confirmed as the amorphous SiO\(_2\) band (SiO\(_2\) standard) that resulted without any indication of crystallization. Figure 3. IR spectra of modified silica nanoparticles

The effect of superhydrophobic silica nanoparticles was demonstrated by dip-coating the glass substrates into the solution. To form the thin film of modified silica nanoparticles, the glass substrates were heated at 100 °C to remove the alcohol solvents. The water contact angles were 137.9 ± 1.2°, 153.7 ± 2.9°, and 135.7 ± 1.0° for alcohol solvents of methanol, ethanol, and 2-propanol, respectively, as shown in Figure 5. The existence of different particle sizes and particle size distributions under different hydrophobic conditions affected the water contact angle with roughness of the surface due to nanoscale particles [35]. The water contact angle was related to the homogeneous surface, which strictly was a function of the tension between liquid and solid surfaces. It is clear that in the ethanol solvent, the water contact angle was the highest as a result of the monodispersity and uniformity of particle size (Figure 2b). Although the particle size distribution of silica nanoparticles in the 2-propanol solvent can be considered more homogeneous than in the methanol solvent, the water contact angle of silica nanoparticles synthesized in methanol was higher. It was confirmed that nanoscale structure contributed toward roughness and, consequently, toward the water-repellent effect. The roughness of the surface increased due to particle size and silica distribution; so, hydrophobic properties occurred on the surface of the material [36].

In order to confirm the superhydrophobic effect of silica nanoparticles, the optimum result from the previous experiment – silica nanoparticles synthesized in ethanol solvent – was applied to the bitumen as both coating and mixing. Figure 6 shows the water contact angle that was dropped into the bitumen, without and with modified silica nanoparticles. In the case of unmodified silica nanoparticles in the bitumen as shown in Figure 6a, the water contact angle was about 89.80°. Meanwhile, in the presence of modified-silica nanoparticles as
can be seen in Figure 6(b) (coating) and 6(c) (mixing), the water contact angle was increased to 149.2° and 148.1°, respectively. In Figure 6(d), it is clear that the modified silica nanoparticles caused roughness to the bitumen surfaces, which contributed to the superhydrophobic effect [36]. Thus, as expected, the modified silica nanoparticles were excellent for the performance of water-repellent surfaces by depositing into the bitumen. Another interesting result was that the products of coating and mixing did not show any significant results, the water contact angles differing by no more than 1.1°. Although bitumen is a hydrophobic material due to its composition consisting of naphthenic acid, other mineral aggregates are hydrophilic, so that the condition is fundamentally incompatible to provide a superhydrophobic effect [37]. Therefore, it can be concluded that modified silica nanoparticles can be used for the large-scale fabrication of superhydrophobic surfaces on the bitumen, which can protect the degradation of the bitumen on the road. However, a further study to evaluate the stability and durability of the superhydrophobic effect on the bitumen surfaces is required.

4. Conclusion

Superhydrophobic silica nanoparticles were successfully synthesized from silica sand, prepared by mechanical milling and the sol–gel method. The particle size and particle size distribution of silica nanoparticles were evaluated with various solvents. Although the smallest particle size was obtained in the methanol solvent, the homogeneous size of the particles were obtained in the ethanol solvent. This result was confirmed by the zeta potential and particle size distribution, which indicated that the silica nanoparticles in the ethanol solvent tended to resist aggregation. Meanwhile, the silica nanoparticles in the 2-propanol solvent showed uniformity like those synthesized in the ethanol but with a larger particle size. It was observed that the size and size distribution of nanoparticles offered different conditions of hydrophobic effects, which showed a maximum of the water contact angle of 153.7 ± 2.9° in the modified silica nanoparticles synthesized in the ethanol solvent, in comparison with the 137.9 ± 1.2° and 135.7 ± 1.0° water contact angles in methanol and 2-propanol, respectively. Based on such an optimum result, application was made to the bitumen both under the coating and mixing method, in which case the water contact angle resulting on the bitumen’s surface indicated that modified silica nanoparticles were excellent for water-repelling performance. In summary, silica sand is an alternative source to synthesize silica nanoparticles that can be used as superhydrophobic material as reported in this study.

Acknowledgments

The authors would like to express gratitude to Indonesia
Disclosure statement

No potential conflict of interest was reported by the author(s).

References

[1] Feng X, Jiang L. Design and creation of superwetting/antiwetting surfaces. Adv Mater. 2006;18 (23):3063–3078.
[2] Callies M. Que re’ D. On water repellency. Soft Mater. 2005;1(1):55–61.
[3] Ke Q, Fu W, Wang S, et al. Facile preparation of superhydrophobic biomimetic surface based on octadecyltrichlorosilane and silica nanoparticles. ACS Appl. Mater. 2010;2(8):2392–2398.
[4] Crick CR, Parkin IP. A single step route to superhydrophobic surfaces through aerosol assisted deposition of rough polymer surfaces: duplicating the lotus effect. J Mater Chem. 2009;19(8):1074–1076.
[5] Kang SM, You I, Cho WK, et al. One-step modification of superhydrophobic surfaces by a mussel-inspired polymer coating. Angew Chem Int Ed. 2010;49 (49):9401–9404.
[6] Liu X, Zhang J, Yang T, et al. Self-assembled hierarchical flowerlike ZnO architectures and their gas-sensing properties. Powder Technol. 2012;217:238–244.
[7] Cheng C, Fan HJ. “Branched nanowires: synthesis and energy applications. Nano Today. 2012;7(4):327–343.
[8] Sun XL, Fan ZP, Zhang LD, et al. Superhydrophobicity of silica nanoparticles modified with polystyrene. Appl Surf Sci. 2011;257(6):2308–2312.
Figure 6. Water contact angles into the bitumen (a) without modified-silica nanoparticles, (b) coated with modified silica nanoparticles, and (c) mixed with modified silica nanoparticles, and (d) comparison of the results without and with modified-silica nanoparticles.

[9] Dubov AL, Perez-Toralla K, Letailleur A, et al. Superhydrophobic silica surfaces: fabrication and stability. J. Micromech Microeng. 2013;23(12):125013.
[10] Gurav AB, Xu Q, Latthe SS, et al. Superhydrophobic coatings prepared from methyl-modified silica particles using simple dip-coating method. Ceram Int. 2015;41(2):3017–3023.
[11] Zha J, Roggendorf H Sol–gel science, the physics and chemistry of sol–gel processing, (Eds.), Brinker CJ, Scherer GW, Academic Press, Boston 1990, xiv, 908 pp., bound— ISBN 0-12-134970-5. Adv Mater. 1991;3:522.
[12] Gao L, He J. Surface hydrophobic co-modification of hollow silica nanoparticles toward large-area transparent superhydrophobic coatings. J Colloid Interface Sci. 2013;396:152–159.
[13] Xue CH, Jia ST, Zhang J, et al. Large-area fabrication of superhydrophobic surfaces for practical applications: an overview. Sci Technol Adv Mater. 2010;11(3):033002.
[14] Awais M, Jalil M, Zulfiqar U, et al. A facile approach towards fabrication of super hydrophobic surface from functionalized silica particles. IOP Conference Series: Materials Science and Engineering, National Centre for Physics, Islamabad, Pakistan: IOP Publishing. 2016:12022.
[15] Moritoki M, Mori T, Shirakura A, et al. Gas barrier property of silica-based films on PET synthesized by atmospheric pressure plasma enhanced CVD. Surf Coat Technol. 2016;307:1070–1073.
[16] Nagasawa H, Yamamoto Y, Tsuda N, et al. Atmospheric pressure plasma-enhanced chemical vapor deposition of microporous silica membranes for gas separation. J Membr Sci. 2017;524:644–651.
[17] Aubert T, Grasset F, Mornet S, et al. Functional silica nanoparticles synthesized by water-in-oil microemulsion processes. J Colloid Interface Sci. 2010;341 (2):201–208.
[18] Tadjarodi A, Haghverdi M, Mohammadi V. Preparation and characterization of nano porous silica aerogel from rice husk ash by drying at atmospheric pressure. Mater Res Bull. 2012;47(9):2584–2589.
[19] Daud FDM, Johari IH, Jamal AHA, et al. Preparation of nano-silica powder from silica sand via sol-precipitation method. AIP Conference Proceeding, Kelantan, Malaysia. 2019;020002:1–4.
[20] Manchanda CK, Khaival R, Mor S. Application of sol–gel technique for preparation of nanosilica from coal powered thermal power plant fly ash. J Sol-Gel Sci Technol. 2017;83(3):574–581.
[21] Rahman IA, Padavettan V. Synthesis of silica nanoparticles by sol-gel: size-dependent properties, surface modification, and applications in silica-polymer nano-composites review. J Nanomater. 2012;2012(10):1–15. 1155:132424.
[22] Ismail A, Alam Syah IA, Kholid M, et al. The effect of milling time on the size of silica particles from silica sand. Mater Sci Forum, Seoul, South Korea. 2017;917:162–166.
[23] Affandi S, Setyawana H, Winardi S, et al. A facile method for production of high-purity silica xerogels from bagasse ash. Adv Powder Technol. 2009;20(5):468–472.
[24] Thuadaj N, Nuniya A. Preparation and characterization of faujasite using fly ash and amorphous silica from rice husk ash. Procedia Eng. 2008;35:206–211.
[25] Munasir A, Hidayatullah M, Triwikantoro ZM, Darminto. sintesis silika amorf dari bahan alam lumipar sidoarjo dengan metode kopresipitasi. SNF Proceeding, UNNES, Semarang, Indonesia. 2010;FM101:1–6.
[26] Zulfiqar U, Subhani T, Husain SW. Synthesis of silica nanoparticles from sodium silicate under alkaline conditions. J Sol-Gel Sci Technology. 2016;77(3):753–758.
[27] Isobe H, Utsumi S, Yamamoto K, et al. Micropore to macropore structure-designed silicas with regulated condensation of silicic Acid Nanoparticles. Langmuir. 2005;21(17):8042–8047.
[28] Rao KS, El-Hami K, Kodaki T, et al. A novel method for synthesis of silica nanoparticles. J Colloid Interface Sci. 2005;289(1):125–131.
[29] Munasir A, Sultan, Triwikantoro M, Zainuri, and Darminto. Synthesis of silica nanopowder produced from Indonesian natural sand via alkali fussion route. AIP Conference Proceedings, Central of Kalimantan, Indonesia. 2013;1555:28.

[30] Wahyudi A, Nurasid T, Rochani S. Preparation of nanoparticle silica from silica sand and quartzite by ultrafine grinding. Proceeding of International Conference on Chemical and Material Engineering, Semarang, Indonesia. 2012;MSD.06:1–7.

[31] James SL, Adams CJ, Bolm C, et al. Mechanochemistry: opportunities for new and cleaner synthesis. Chem Soc Rev. 2012;41:413–447.

[32] Buining PA, Liz-Marzan LM, Philipse APA. Simple preparation of small, smooth silica spheres in a seed alcohol for stober synthesis. J Colloid Interface Sci. 1996;179(1):318–321.

[33] Hristov DR, Rocks L, Kelly PM, et al. Tuning of nanoparticle biological functionality through controlled surface chemistry and characterisation at the bioconjugated nanoparticle surface. Sci Rep. 2015;5(1):17040.

[34] Wu C, Liu Q, Liu J, et al. Hierarchical flower like double-layer superhydrophobic films fabricated on AZ31 for corrosion protection and self-cleaning. New J Chem. 2017;41(21):12767–12776.

[35] Simpson JT, Hunter SR, Aytug T. Superhydrophobic materials and coatings: a review. Rep Prog Phys. 2015;78(8):086501.

[36] Ghio S, Paternoster G, Bartali R, et al. Fast and large area fabrication of hierarchical bioinspired superhydrophobic silicon surfaces. J Eur Ceram Soc. 2016;36(9):2363–2369.

[37] Baghshaw S, Kemmitt T, Brooke S, et al. Hydrophobic chemical treatment of aggregate surfaces to re-engineer the mineral/bitumen interface and improve bitumen adhesion, Road Mater and Pavement Des. 2015;16:19–30.