Hydrophobic Nanoparticles-Silica from Natural Sands with TMCS as Media

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Abstract. The purpose of this research is to synthesize hydrophobic silica nanoparticles (NPS). Modified mixtures of trimethylchlorosilane (TMCS) and NPS are the focus of the analysis of the nature of hydrophobicity. 0.5g of silicon dioxide (SiO 2) powder was mixed with TMCS, then coated on a glass substrate using the spin-coating method. Furthermore, the glass was put in a heating oven for one hour, at 65°C. In addition to the hydrophobicity test, morphological analyses using SEM (scanning electron microscopy) were also carried out. The contact angle of 115.6˚ indicates a hydrophobic nature. The presence of homogeneous NPS SiO 2 in the TMCS solution affects the hydrophobic quality of glass surfaces coated with NPS.

Keywords NPS, hydrophobic, TMCS.

1. Introduction
Silica has the advantages of physical and chemical properties, with extensive application prospects in various fields. Silica is the primary ingredient in glass and the glass industry as well as solar cells [1], in the form of silica and calcium nanocomposites as bioactive material candidates for bone tissue repair applications[1], [2]. Other uses of silica nanoparticles (NPS) are industrial applications related to the production of pigments, pharmaceuticals, ceramics, and catalysts [3], together with superparamagnetic materials, magnetite (Fe 3 O 4) can be applied in drug delivery systems (DDS) [4]. In nature, silica is the most commonly occurring compound, constituting 60.6% of the earth’s crust. Silica can be sourced from natural mineral materials such as quartz sand, diorite stone, clay, and so on, while the organic material can be extracted from rice husk ash, bagasse-ash, and such [5].

Special treatment is required in synthesizing SiO 2 silica to a nanometer order size. Some often used methods of silica NPS synthesis include the gas phase process, emulsion techniques, and the plasma spraying and fogging process polymerization of dissolved silica into organosilica. NPS synthesis can also be done using the co-precipitation method [1], [6], sol-gel [7], [8], the wet chemical reaction method [9], the continuous method [4], [10], and the sol-gel method process [11]. The co-precipitation method is a method of synthesizing inorganic compounds, based on the deposition process of more than one substance together when it passes the saturation point. This method takes a relatively short duration of ± 12 hours, at low temperatures and utilizes tools and materials that are easily obtained, so that the synthesis process can be carried out flexibly[6], [12]. Synthesized SiO 2 was obtained from Purus beach sand (SiO 2, Wt. 71%), and the size of the nanoparticles produced was 2–80
nm and of high purity [5]. Up to 98% silica can be extracted and obtained from rice husk material [13] and sugarcane ash and of nanometer order particle size [14]. Hydrophobic NPS synthesis for glass coating can be made from basic ingredients, such as DEODMS, MTEOS, TEOS, and TPOZ as precursors. These synthetic precursor materials are not economically effective and have a toxic effect. On the other hand, NPS from natural materials can be extremely beneficial, because it is very cheap, easy to obtain, and environmentally friendly.

NPS-hydrophobicity coated glass can provide it with water repelling and anti-snow properties, so that dirt doesn’t easily attach to it (self-cleaning), proving more beneficial to humans[15]–[17]. With a thin layer of NPS-hydrophobia on the glass surface, water droplets on the glass form a perfect sphere. This causes the dirt on the glass to be carried away by the droplets of water that glide on the glass, and this finding is predicted to have an extensively beneficial impact. This self-cleaning attribute can also be applied to the functional glass separating liquids, biomedical equipment, decreasing the rate of turbulence in water pipes, and, most interestingly, it can be used as the anti-corrosion surface for transportation to space [18], [19].

If the hydrophobicity angle is > 90°, then the NPS is hydrophobic. In previous studies, NPS with water glass precursors and dip-coating method obtained a hydrophobicity angle of 118°, at a heating temperature of 50°C (Chen et al., 2016; Rahman & Padavettan, 2012) and coating with pyrophyllite mineral, using the spin coating method with heating 65°C, obtained a hydrophobic angle of 142.5° [20][8][21]. Using the description above, the focus of this research is the synthesis of silica NPS from quartz sand materials, which contain 70% SiO$_2$. The continuous method (hydrothermal-precipitation) is a simple synthesis method, chosen for the extraction and synthesis of natural material-based NPS [9], [22], [23]. Furthermore, the NPS powder obtained was modified using the TMCS solution and using the spin coating method coated on the glass surface, after which a hydrophobic nature test was carried out. Characterization of samples, with angle tests (hydrophobicity properties), x-ray diffraction (XRD) for phase analysis and structure, and SEM for morphological analysis were also carried out.

2. Materials and Method
2.1. Materials
The materials used in this study include silica sands (taken from Bancar-Tuban area, Indonesia), hydrochloric acid (HCl) (2M), DI-water (H$_2$O), sodium hydroxide (NaOH) (7M), TMCS, and glass preparations. The equipment used included cup and mortar, cup glasses (50 ml, 100 ml, 250 ml, 500 ml), measuring cups, metal spatulas, glass spatulas, pipettes, glass funnels, filter paper, magnetic stirrers, analytical scales, and a furnace. The stages of work were as follows: Finely ground silica sand obtained using plates and mortars and sieving. Sand is soaked using HCl (pro-analyst, 37%) for two hours to remove impurities in the quartz sand. Then the quartz sand powder was washed with H$_2$O to remove the HCl and then dried.

2.2. Synthesis and Characterization
Following this, the sand powder was prepared. 10g of it was taken and mixed with solid NaOH (7M), then sterilized for 2 hours, at a temperature of 80-90°C, to form a solid phase sodium silicate solution (Na$_2$SiO$_3$). 0.5 grams of NPS powder was taken and mixed with TMCS, at concentrations of 1 M, 1.5 M, and 2 M; previously the TMCS was dissolved with n-hexane, where the mixing process was carried out for 13 hours using the water bath shaker media and then left at room temperature for 24 hours to become NPS gel. NPS/TMCS coating on the glass was carried out using the spin coating method, that is by dropping the substrate of the preparation on the glass, placed on the rotating disk. Glass coated with NPS/TMCS was then heated at 65°C for 1 hour, and then it was ready to be tested for its hydrophobicity, crystal structure, and microstructure with XRD and SEM-EDX.

2.3. The Glasses Modification with TMCS and NPS
The glass substrate coating was done using the main material TMCS as a matrix and the silica as a filler. 0.5 g silica powder was mixed into TMCS, with a molarities of 1M, 1.5M, and 2M (shown in Figure 1), which had previously been dissolved with n-hexane, using a stirrer for 15 minutes. The
TMCS/SiO$_2$ was mixed using a water bath shaker media for 13 hours, at a temperature of 30$^\circ$C, until the solution was homogeneous. Mixing of TMCS with SiO$_2$ occurs using the following reaction [2][24].

![Figure 1](image1.png)

**Figure 1.** Result of TMCS/SiO$_2$ mixed: (a) TMCS 1M , (b) TMCS 1.5M , and (c) TMCS 2M.

Before coating, the glass was prepared by first washing with and soaking it in alcohol for 15 minutes, to remove any traces of dirt on the glass. The glass substrate coating process used the spin coating method for 15 seconds, at a speed of 1000 rpm. Then the sample was heated using a furnace for 1 hour, at a temperature of 65$^\circ$C (Figure 2). A drop test was carried out on each sample to determine their hydrophobicity properties.

![Figure 2](image2.png)

**Figure 2.** Layer on glass substrate: (a) TMCS 1M , (b) TMCS 1.5M , and (c) TMCS 2M.

3. Result and Discussion

3.1. Synthesis of NPS

The silica powder was obtained from silica sands. The content of SiO$_2$ found in surfing sand is around 70% [5]. For the silica synthesis process in this study, the method used was the continuous method. In general, the co-precipitation method produces smaller and similar particle sizes. In the process of synthesizing silica, silica sand is first soaked using 4M HCl, to remove the metal elements present in the sand. Subsequently, the sand is dissolved using 7M NaOH up to as much as 60 ml, until the sodium silicate (Na$_2$SiO$_3$) solution is formed.

Furthermore, the Na$_2$SiO$_3$ glass water solution was titrated using 2M HCl, until the coprecipitation result was obtained: Si(OH)$_4$ slurry. Titration was carried out in stages, while the stirring was carried out until a homogeneous solution was obtained and the pH of the solution approached 7. The final product of the Si(OH)$_4$ slurry was white, which was then dried in an oven at a temperature of 100$^\circ$C, until a white SiO$_2$ powder was obtained (Figure 3).
3.2. X-Ray Diffraction Analysis

Based on the NPS synthesis, a characterization test using X-ray diffraction (XRD) was carried out, and the diffraction pattern was analyzed using the Match! software. The NPS had an amorphous phase, and no crystal peaks were formed. The peak width was at an angle of $2\theta = 26.58^\circ$, which indicated that the sample was still amorphous. The diffraction peak profile follows results obtained in previous studies [5]. This amorphous phase was suspected, because the NPS formation process still used a low temperature hydrothermal ($T< 500^\circ C$), and co-precipitation ($< 100^\circ C$). While, it is known that the transition temperature of the crystalline phase change in SiO$_2$ (quartz, tridymite, and cristobalite) is within the range of $360–1665^\circ C$ temperature [17], [25]. Shown in Figure 4, XRD patterns from NPS samples were synthesized, with diffraction angles between $5-100^\circ$ and broad peaks.

![X-ray Diffraction](image)

**Figure 4.** The pattern of X-ray Diffraction of amorphous silica

3.3. The Contact Angle Analysis

The level of wetness of a surface can be determined from the angle formed with the water dripped on the substrate. The substrate used was prepared glass. The contact angle formed was obtained by dripping water on the glass substrate, photographed using a Canon IXUS digital camera. Then the photos were determined by the angle of contact using the Photoshop CS5 software. The difference in contact angles between the prepared before and after TMCS/NPS coats, in theory, show differences in water contact existing on the surface coated and uncoated using TMCS/NPS. The SiO$_2$ content in the hydrophobic solution can increase surface roughness, so that it is capable of resisting
water. From this research, the contact angle values were obtained for each sample of different TMCS molarity.

![Figure 5. Differences in droplets on the glass surface: (a) before, (b) after coated with TMCS/NPS](image)

![Figure 6. The contact angle samples: (a) TMCS 1M, (b) TMCS 1.5M, and (c) TMCS](image)

In the sample with 1M molarity, the contact angle was 51.6°, the sample with 1.5M molarity obtained the most significant contact angle as compared to the two examples, which was 115.6°. The sample with the 2M molarity formed a contact angle of 100.9°. While the measurement of the contact angle using the tangential line equation (1), obtained the largest angle 115.5°, in the sample with a TMCS molarity of 1.5M. From the two methods used, the resulting contact angle has a very small difference in value. A surface can be said to be hydrophobic if the contact angle produced is > 90°. If the contact angle produced is > 50°, the surface is super hydrophobic, while the surface with a contact angle < 90° is hydrophilic. From the results of the contact angle above, good hydrophobic properties exist in samples with TMCS molarity of 1.5M, where the hydrophobicity for 2M molarity is lower than 1.5M. This is due to the lack of mixing time in the solution shaker water bath, such that the SiO₂ particles in the sample with 2M TMCS are less homogeneous. Moreover, the higher the temperature used when mixing, the larger the contact angle (Affandi et al., 2009). In the research and surface modification using TMCS, the contact angle of 166° [2], [8] was obtained, because the TMCS solution can react with silica to produce a nonpolar solution, which causes the surface to have
hydrophobic properties. Modification of a surface using TMCS has become the standard for creating a hydrophobic layer [2], [26].

The measurement of the contact angle using the tangential line equation (1), obtained the largest angle at 115.5\(^\circ\), in the sample with a TMCS molarity of 1.5M. From the two methods used, the resulting contact angles carry a very small difference in value. The determination of possible contact surface hydrophobic angles can be done using the tangential lines the equation. The first step is pressing the liquid on the surface and then taking a picture of the water droplet. The next step is to draw the edge of the droplet’s interface with the surface water substrate. Then the height (h) and width (w) of the water droplets can be measured. The value of the contact angle can be calculated using equation 1 [27].

\[
tan \frac{\theta}{2} = \frac{2h}{w}
\]

![Illustration of tangential line equation](image)

**Figure 7.** Illustration of tangential line equation

### 3.4. The Morphological Analysis using SEM

The coating process of TMCS/NPS on the substrate was carried out using the spin coating method. The distribution of SiO\(_2\) particles that spread on the substrate can be seen in morphological testing, using the SEM (scanning electron microscope). Based on the results of the SEM test, with 1500x magnification on a 10\(\mu\)m scale, it was seen that the distribution of NPS was less homogeneous, yet it still contained hydrophobic properties, because the layer was spread evenly on the surface. This is caused due to the spreading of NPS less evenly distributed in the TMCS solution during mixing. Factors that affect them are long and large temperatures, used for mixing NPS with TMCS in the water bath shaker media. The distribution of SiO\(_2\) particles in nanoparticle size makes the substrate coarse, as compared to microparticle SiO\(_2\) [26]. The roughness of a substrate affects the nature of the hydrophobic substrate because a high level of roughness on the surface will result in a higher contact angle. A hydrophobic solution coating on a substrate can modify the surface, such that the surface has polar properties [17]. In this case, there is excellent adhesion, as compared to the cohesion, on a hydrophobic surface [24].
4. Conclusions

Based on the results of the research and the earlier discussion, the following can be concluded: (i) Synthesis of NPS from silica sands using the co-precipitation method was obtained, with amorphous phase silica so that could be used as filler on thin layer substrates; (ii) NPS, which was mixed with TMCS and coated the substrate, made the substrate nonpolar. Thus, the substrate will tend to have hydrophobic properties. The nature of the hydrophobic glass substrate can be determined through the contact angle produced. Based on the research, the most significant contact angle obtained was 115˚, with a TMCS molarity of 1.5 M.

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