Utilization of sodium silica from coal fly ash and trimethylchlorosilane as self-cleaning coating on glass

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Abstract. Sodium silica is extracted from coal fly ash generated from the power plant. Furthermore, sodium silica is utilized as silica sol, and then it is added to the coating solution with trimethylchlorosilane (TMCS) as an additive. The coating solution is applied to the glass surface by the deep coating method in order to get a self-cleaning glass. This material is usually used as microfluidic devices for biotechnology or bioprocessing. This study aims to analyze the effect of various volume ratios of silica sol and silane sol from TMCS on the physicochemical characterization of the glass surface. The ratios used between silica sol and silane sol are 1:0, 1:1, 1:2, 1:4, and 1:8. Wettability, hysteresis, morphology, and functional group analysis are conducted on the coated glass. The best concentration ratio is 1:8 that produces a contact angle of 107.53°, contact angle hysteresis of 3.13°, and transparency of 99.04%. Moreover, the glass-coated by silica sol-silane sol has surfactant resistance. When Sodium Dodecyl Sulfate (SDS), at a concentration of 2 times of CMC, is dropped on the glass surface inclined at 10°, the droplet slides without leaving a trace. It can be concluded that the glass coated by sodium silica and TMCS has a self-cleaning characteristic.

1. Introduction
The microfluidic device is applicable to various fields, especially in biotechnology and bioprocessing. Generally, microfluidic is used to reduce the cost and time required in process development [1]. In biotechnology segments, microfluidic employs small volumes of liquids, and then it analyses single or multi-cell in dynamic conditions. The examples are included microfluidic application in enzyme, mammalian cell, and microbial cell studies, particularly in cell screening and separation systems, enzymatic reactions, bacterial culture, and protein analysis [2-4]. As bioprocessing is a scaling up of biotechnology, microfluidic is utilized in top-down and bottom-up paradigms, like as microbioreactor and evaluation of cell characterization, respectively [5].

Several materials that can be used as microfluidic materials are silicon fabrications like glass and silicon wafer, polymers like poly(dimethylsiloxane) and poly(methylmethacrylate), as well as metallic fabrication [1,6]. Glass is inert and has optical transparency, and it is suitable material for high temperature and pressure involved in process. This material belongs to inorganic materials that have good surface stability, tunable thermal conductivity and solvent compatibility [7], thus is chosen as material for microfluidic.

However, the presence of fouling leads to declining microfluidic performance, particularly when microfluidic is used as biological analysis. Several methods are developed to handle fouling in microfluidic, like surface patterning using photolithography or soft lithography [8,9], or surface modification by changing the surface wettability. The latter method is usually associated with self-cleaning surface, that is explained as a surface with capability to prevent or reduce surface contamination.
Self-cleaning process is affected by adhesion reduction of the attached particles on the surface, and increased mobility of the droplets that removing particles [11]. Therefore, self-cleaning mechanism can be conducted through hydrophilic or hydrophobic surfaces. Nevertheless, previous study shows that the percentages of particle removal for hydrophilic and superhydrophobic surfaces are 41% and 98%, respectively [12]. Hence, it can be concluded that hydrophobicity synergized with self-cleaning performance.

Formerly, a glass with a hydrophobic surface is obtained by combining fluorine, silica, and tetraethoxysilane (TEOS) [13]; however, fluorine is a toxic substance when released into the environment as well as it can last a long time-then be accumulated inside organisms. Hence, a prior study results that silica-based compounds are proven to be able to replace fluorinated compounds as hydrophobic agents with adhesive agents as an additive. Silica can be extracted from biomass or waste; hence the utilization of waste leads to a useful waste handling. One of the solid wastes that contain silica is coal fly ash. This material, which has a fine grain size, is generated from the combustion of coal in a power plant [14]. In Indonesia, the production of fly ash increases annually, in accordance with the consumption of coal as a raw material for the power plant industry [15]. Recently, coal fly ash has been disposed of in off-site or on-site landfills without further treatment. Therefore, the utilization of coal fly ash is necessary to reduce the landfill volume. Besides, the addition of an adhesive agent increases surface hydrophobicity. TEOS has been used as an adhesive agent for several studies [16-18], with water Contact Angle (CAs) between 116° to 157.2°. However, TEOS is expensive and not environmental-friendly. The other alternative is using trimethylchlorosilane (TMCS) as modifying agent. The alkyl groups from TMCS replace H atom in silanol groups on the surface of glass, thus hydrophobicity of glass surface increases [19]. The application of TMCS as adhesive agent in silica-based materials shows hydrophobic CA of 118° [19] and 115° [20].

In this study, silica is synthesized from coal fly ash as sodium silicate. Then, TMCS is added in various amounts to the sodium silicate to produce the coating solution. The coating processes of glass that are popularly used are Chemical Vapor Deposition (CVD), spray coating, spin coating, and dip coating. CVD method can produce a uniform layer [21], even so it needs a vacuum chamber that is difficult to handle. Thus, the dip-coating method is used because it can produce thin layers from chemical solutions with low-cost and waste-free processes [22]. The optical, wettability, functional group, and morphology analysis are conducted on the variables. Then the coated glasses resistance to a low surface tension liquid is tested. Sodium Dodecyl Sulfate (SDS) in various concentrations is used as surfactant drop. The result shows whether the self-cleaning mechanism of coated glasses declines due to the presence of surfactant.

2. Materials and method

Coal fly ash was obtained from a power plant in Balikpapan. Ethanol 99.8% and 4 M sodium hydroxide (NaOH) were from Smartlab, while 4 M hydrochloric acid (HCl) was purchased from Buanalab. The other materials are TMCS was from Merck, distilled water, and glass slide GEA medical 7105 with the dimension of 25.4 mm x 76.2 mm x 1.0 mm.

2.1. Synthesis of sodium silicate from coal fly ash

The composition of fly ash was analyzed by X-ray Fluorescence (XRF). This step was conducted parallely with the synthesizing process of sodium silicate. Fly ash was washed using hot water at 100°C to remove impurities, then filtered and dried. After that, the fly ash was pre-treated with 4 M HCl concentration, and then the mixture was neutralized with the addition of water, filtered, and washed again with water. A high concentration of HCl is used to remove metallic and non-metallic oxide impurities, as well as affect the purity of silica. Then the residual solid was dried at 100°C for 3 hours. The dried sample was then added with 4 M NaOH solution, then stirred with a magnetic stirrer at 150 rpm for 3 hours on a hotplate at 70°C. Finally, the filtrate and the residue are separated so that the yield is a sodium silicate solution [23].
2.2. Preparation of coating on the glass
Initially, a mixed solution of TMCS/ethanol was produced with the volume ratio of TMCS to ethanol of 2:3. Originally, TMCS has a low flash point, and it is reactive with water. To decrease the flashpoint, TMCS should be dissolved in an organic solution [23] [24]. Then, TMCS solution or silane is added to natrium silicate solution or silica sol. In a previous study, the various volume ratios produced between sol silica and sol silane are 1:0, 1:1, 1:2, 1:4, 1:8 [23]. Each sample has its own nomenclature as stated in table 1.

| Samples | Nomenclatures |
|---------|---------------|
| 1:0     | A             |
| 1:1     | B             |
| 1:2     | C             |
| 1:4     | D             |
| 1:8     | E             |

Table 1. The nomenclatures of the samples.

Before coating, the glass was washed with soap and then sterilized by immersing it in 99.8% ethanol for 1 hour. The next step is the glass was sonicated with an ultrasonic bath cleaner containing distilled water for 30 minutes. After that, both surfaces are dried in a vertical position. The coating method used on glass was dip coating. The sterilized glass substrate was immersed in a mixture of silica sol and silane sol for 24 hours, followed by drying in an oven at 100°C for an hour [19].

2.3. Physical analysis
The transparency of coated glasses was measured using UV-Vis Spectrophotometer with a wavelength of 420 nm. Equation (1) was used to obtain the transparency percentage of the glass.

\[
\% \text{Transparency} = \frac{\% \text{Transmittance of coated glass}}{\% \text{Transmittance of uncoated glass}} \times 100\%
\] (1)

The wettability of the glasses’ surface was determined by deposing water droplet on the horizontal glass surface in ambient conditions [25]. The CA was measured using Image J software. While for adjusting the self-cleaning properties, the Contact Angle Hysteresis (CAH) was tested on the glass surface. The CAH was determined using the inclined plane method. A maximum value of stable CA is defined as advancing contact angle \(\theta_a\), whilst receding contact angle \(\theta_r\) is a minimum stable contact angle. The advancing contact angle can be observed before the contact line begins to move outward the inclined plane, in contrast, \(\theta_r\) is obtained before the contact line starts to move inwardly. Moreover, contact angle hysteresis is the difference between advancing and receding contact angles [26].

\[
\text{CAH} \equiv \Delta \theta = \theta_a - \theta_r
\] (2)

A water droplet of 20 \(\mu\)l was deposited on the surface under the tilt angle of 10° [27]. The following steps were examined the functional group and surface morphology of the best results using Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM), respectively.

2.4. The experiment of various SDS concentrations on self-cleaning properties of coated glasses
The aqueous surfactant solutions were made using SDS with several concentrations. They are 2.05, 4.10, 8.20 (CMC), and 16.40 (2 times CMC) mM. Then, 20 \(\mu\)l of surfactant solutions were dropped on the horizontal coated glass to measure the CA. The last step was determining the CAH using the same method as the water droplet [26].
3. Result and discussion
Based on XRF analysis, the coal fly ash contains iron (Fe), Calcium (Ca), Silicon (Si), Aluminium (Al), Sulfur (S), Kalium (K), and Manganese (Mn). The detailed composition is shown in table 2.

| Components | Percentage (%) |
|------------|----------------|
| Fe         | 52.06          |
| Ca         | 20.10          |
| Si         | 11.60          |
| Al         | 5.60           |
| S          | 1.40           |
| K          | 1.20           |
| Mn         | 0.70           |

It is shown that the coal fly ash contains Silicon with 11.6%. This component is one of the main atoms to form sodium silicate by reacting the pre-treated fly ash with NaOH. Sodium proton from dissociated NaOH will bind to unstable SiO$_3^{2-}$ to produce brownish-yellow sodium silicate.

3.1. Transparency test
Based on direct observation in figure 1, the coating with natrium silicate-silane sol has no effect on glass transparency. Then, the transparency results using UV-Vis Spectrophotometer are collected as a graph in figure 2. Glass coated only with silica sol, or sample A has a transparency of 85.13%, and glass coated with a mixture of silica sol-silane sol in a ratio of 1:8 or sample E has a transparency of 99.04%. The increase in the percentage of transparency is caused by increasing the volume of TMCS solution, even the increment is not significant. This result is in accordance with Hamidah et al. [19].

**Figure 1.** (a) Uncoated glass, (b) glass with sodium silica coating or sample A, (c) glass with a coating of 1:1 volume ratio of sodium silica-sol silane ratio or sample B, (d) glass with a coating of 1:2 volume ratio of sodium silica-sol silane ratio or sample C, (e) glass with a coating of 1:4 volume ratio of sodium silica-sol silane ratio or sample D, (f) glass with a coating of 1:8 volume ratio of sodium silica-sol silane ratio or sample E.
3.2. Wettability and self-cleaning properties

In this study, the glass that has been coated with silica sol-silane sol gains a larger contact angle than the uncoated glass. However, when glass was coated with sodium silicate only, it resulted in a hydrophilic surface with a CA of 6.53°. It is because sodium silicate can adsorb moisture in the surrounding environment, hence the OH group on sodium silicate bonds with hydrogen atoms from moisture to form H₂O. The following figure 3 shows the results and pictures of the CA measurement on various glass variables. Furthermore, sample E results in the largest CA of 107.53°. The increase in CA that occurs with each addition of the silane sol volume in the silica sol is caused by a (CH₃)₃SiCl compound that belongs to TMCS. The (CH₃)₃Si group of this compound can bind to the Si-O group on sodium silicate, resulting in a hydrophobic layer.

Figure 2. The relation between transmittance and transparency of glass.

3.2.1. Contact angle hysteresis (CAH) test

The results of the contact angle hysteresis (CAH) test were obtained as shown in figure 4. Figure 4 (a), which is ordinary glass, has a CAH of 11.6°. The shape of the droplet on uncoated glass is asymmetrical when placed on an inclined plane. This is due to a defect on the glass surface, thus when the water flows downward, there is a point of the droplet that blocks on the surface and the water droplet deforms from a semicircle to become slightly elongated. Furthermore, the glass coated with sample E (figure 4 (e)) has a CAH of 3.13°, which is smaller than the CAH on uncoated glass. The higher volume of silane sol mixed with the silica sol resulted in smaller CAH because the hydrophobicity also increased. When the hysteresis angle has a small value or is close to 0°, the droplet shape is symmetrical on the inclined plane and does not elongate. This allows the droplets to roll on the surface of the glass without forming a tail. This phenomenon indicates that the coated glass surface is self-cleaning. In addition, the qualitative investigation of water droplet movement on the 1:8 silica sol-silane sol coated...
glass with various surface inclinations below 10° has been conducted. The result obtained is water droplets can still roll with a minimum sliding angle of 6°.

![Figure 4](image1)

**Figure 4.** The CAH of the water droplet on (a) uncoated glass, (b) glass coated with sample B, (c) glass coated with sample C, (d) glass coated with sample D, (e) glass coated with sample E.

### 3.3. Functional group analysis

In figure 5, the surface that has been coated with silica sol and modified by TMCS as an adhesive agent shows the presence of several functional groups. The groups are shown in table 3. Si-O-Si bonds or siloxane appear in the wave absorption range of 11050-1300 cm. Silane can form siloxane bonds (Si-O-Si) with hydroxyl groups on a surface. The unreacted Si-H group allows further incorporation of functional molecules and self-crosslinking by hydrolysis and condensation reactions to form Si=O-Si bonds [28]. With this bond, it can be concluded that sodium silicate and TMCS as an adhesive agent have been homogeneous and bonded to each other.

![Figure 5](image2)

**Figure 5.** The FTIR result for analyzing functional group on uncoated glass, glass with sodium silicate coating, and glass with sodium silicate and TMCS coating.

### Table 3. The result of functional group analysis [29].

| Functional Group | Wavelength Number (cm⁻¹) |
|------------------|--------------------------|
| Si-H             | 52.06                    |
| Si-CH₃           | 20.10                    |
| Si-OH            | 11.60                    |
| Si-O-Si          | 5.60                     |
| Si-Cl            | 1.40                     |
3.4. Morphology analysis
Based on the results of the SEM in figure 6 with 1000x magnification, it is shown that there are morphological differences produced on the three glass surfaces. In figure 6a, ordinary glass does not clearly show the grain aggregates, hence the grain and layer sizes cannot be determined. In Figure 6b, the glass with sodium silicate coating has a nonuniform deposited layer. The particle shape is not homogeneous, and there are many gaps in the morphology of the sample. The gaps are called voids which can be seen more clearly in figure 7 (a). In this variable, voids are almost present uniformly between the particles. The occurrence of voids in the sodium silicate coating is due to less homogeneous of the particles or elements that consisted in the coating. Furthermore, in figures 6c and 7b, the glass coated with sodium silicate-sol silane has a more uniform deposited layer, as well as has an almost uniform particle shape. The morphology of the resulting layer tends to be denser with fewer voids. This proves that there is a bond between sodium silicate and TMCS as an adhesive agent [30].

![Figure 6](image1.png)

**Figure 6.** Morphological Test Results using SEM on glass surface with 1000x magnification: (a) uncoated glass, (b) glass with sodium silicate coating, (c) glass with sodium silicate and TMCS coating.

![Figure 7](image2.png)

**Figure 7.** Morphological Test Results using SEM on glass surface with 10,000x magnification: (a) glass with sodium silicate coating, (b) glass with sodium silicate and TMCS coating.

3.5. Effect of surfactant on the coated glass slide
Figure 8 shows that the CA of coated glass with sample E has hydrophobic properties when SDS solution is deposited on the surface. However, the results of the CA of SDS are lower compared to the water droplet one. It is also stated that higher surfactant concentration leads to having smaller CA. Both phenomena are associated properties of surfactants. Surfactant has a hydrophilic head and hydrophobic tail that leads to surfactant tendency to converge at the interface and reduce the free energy of the interacted system. Molecule adsorption at the interface is a possible mechanism responsible for the decrement of free energy. However, when the interface is saturated, the overall energy reduction continues through several mechanisms, one example is micelles formation [31]. Micelles start to form
when a surfactant is in the critical micelle concentration (CMC). Hence, at the CMC, the surfactant drop has the smallest CA, and his CA is stagnant even the surfactant concentration is increased.

The surfactant droplet deposited on the ordinary glass surface with a tilt angle of 10° undergoes decay, as shown in figure 9. However, the solution does not completely drop because it still forms a tail. This indicates that the surface of the glass is not homogeneous, or there are defects on it. Therefore, it can be concluded that ordinary glass surfaces do not have self-cleaning capabilities. Whereas in figure 10, the surfactant droplet has a small CAH, that is 8.48°, when placed on a glass substrate coated with sample E. The droplet shape still looks symmetrical on an inclined plane, and the droplet does not experience elongation. This allows the droplets to roll over the glass surface without forming a tail. It can be indicated that the coated glass still has self-cleaning properties and has a resistance toward surfactant solution.

Figure 8. Relation among volume ratio of silica sol-silane sol mixture, contact angle, and concentrations of SDS solutions.

Figure 9. SDS drop test results on an uncoated glass substrate with the tilted angle of 10°.
4. Conclusion

The effect of the volume of the silane sol in the silica sol-silane sol mixture increases the hydrophobicity of the glass surface. The volume ratio of silane sol and silica sol that produces the highest CA is 1:8, with a CA of 107.53°. This coated glass variable also exhibits resistance to surfactant solutions. This is indicated by the surfactant solution that can still roll on the surface with a sliding angle of 10° without leaving a water beam or tail on the glass. Glass coated with sodium silicate and TMCS as an additive also has a self-cleaning mechanism because it has CAH below 5° and 10° for water droplet and surfactant drop, respectively.

5. Reference

[1] Marques M P C and Szita N 2017 Curr. Opin. Chem. Eng. 18 61
[2] Oliveira A F, Pessoa A C S N, Bastos R G and de la Torre L G 2016 Biotechnol. Prog. 32 6 1372
[3] Ortseifen V, Vieflues M, Wobbe L and Grünberger A 2020 Front. Bioeng. Biotechnol. 8 589074
[4] Blackburn M C, Petrova E, Correa B E and Maerk I 2016 Nucleic Acids Res. 44 7
[5] Bjork S M and Joensson H N 2019 Curr. Opin. Biotechnol. 55 95
[6] Angelescu D E 2011 Highly Integrated Microfluidics Design (Norwood: Artech House) p 7
[7] Hou X, Zhang Y S, Santiago G T, Alvarez M M, Ribas J, Jonas S J, Weiss P S, Andrews A M, Aizenberg J and Khademhosseini A 2017 Nat. Rev. Mater. 2 17016
[8] Brouch A T and Petkoska A T 2014 Int. J. Eng. Res. Technol. 3 12
[9] Li T, Ren T and He J 2017 The inspiration of nature: natural counterparts with self-cleaning functions Self-cleaning Coatings, Structure, Fabrication and Application ed J He (Cambridge: The Royal Society of Chemistry) chapter 1 pp 1-24
[10] Sun D and Bohringer K F 2019 Micromachines 10 101
[11] Yilbas B S, Hassan G, Al-Qahtani H, Al-Aqeeli N, Al-Sharafi A, Al-Merbari A S, Baroud T N and Adukwu J A E 2019 Sci. Rep. 9 14697
[12] Heckenthaler T, Sadhujan S, Morgenstern Y, Natarajan P, Bashouti M and Kaufman Y 2019 Langmuir 35 48 15526
[13] Brassard J D, Sarkar D K and Perron J 2012 Appl. Sci. 2 2 453
[14] Wardani S P R 2008 (Semarang: Faculty of Engineering Universitas Diponegoro)
[15] Harjiono D 2006 Prosiding Seminar Batubara Indonesia (Yogyakarta)
[16] Widati A A, Nuryono, Kartini I and Martino N D 2017 J. Chem. Technol. Metall. 52 6 1123
[17] Asri Fah and Supari Z A 1 2017 Jurnal Inovasi Fisika Indonesia 6 1 1
[18] Huang Z, Wang F and Li J 2018 IEEE 11th International Conference on the Properties and Applications of Dielectric Materials (ICPADM) 293
[19] Hamidah N, Rizkiyana M F, Setyawan H and Affandi S 2012 Jurnal Teknik POMITS 1 1 1
[20] Munasir and Safitri I 1 2021 IOP Conf. Ser. Mater. Sci. Eng. 1125 012005
[21] Feng J, Gong X, Lou X and Gordon R G 2017 ACS Appl. Mater. Interfaces. 9 12 10914
[22] Grosso D 2011 J. Mater. Chem. 21 43 17033
[23] Widati A A, Nuryono, Aryanti D P, Wibowo M A, Kunarti E S, Kartini I and Rusdiarso B 2018 Indones. J. Chem. 18 4 587

Figure 10. SDS drop test results on glass coated with sample E and tilted angle of 10°.
[24] Zhu L, Wang Y, Cui S, Yang F, Nie Z, Li Q and Wei Q 2018 *Molecules* **23** 1935
[25] Xin B and Hao J 2010 *Chem. Soc. Rev.* **39** 2 769
[26] Young T 1805 *Philos. Trans. R. Soc.* **95** 65-87
[27] Hassan G, Yilbas B S, Al-Sharafi A and Al-Qahtani H 2019 *Sci. Rep.* **9** 5744
[28] Demirci A, Matsui J, Mitsuishi M, Watanabe A and Miyashita T 2013 *Mol. Cryst. Liq. Cryst.* **579** 1 34
[29] Colthup N B, Lawrence H D and Wiberley S E 1990 *Introduction to Infrared and Raman Spectroscopy 3rd ed* (San Diego: Academic Press Inc.)
[30] Sarawade P B, Kim J K, Park J K and Kim H K 2006 *Aerosol Air Qual. Res.* **6** 93
[31] Chen L H and Lee Y L 2004 *AIChE J.* **46** 1 160

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