Synthesis and characterization of hydrophobic silica prepared by different acid catalysts

Linda Karlina\textsuperscript{1,a}, Choiril Azmiyawati\textsuperscript{1,b}, Adi Darmawan\textsuperscript{1,c,*}

\textsuperscript{1} Chemistry Department, Faculty of Science and Mathematics, Diponegoro University, Indonesia  
Email: \textsuperscript{a} lienkar27@gmail.com; \textsuperscript{b} choiril.azmiyawati@live.undip.ac.id; \textsuperscript{c,*} addidarmawan@live.undip.ac.id

Abstract. Silica particles tend to be aggregate and difficult to be dispersed homogeneously in organic coatings or polymer nanocomposites because of the large number of -OH groups in the surface, and this remains an obstacle to further applications. Surface modification was carried out to improve silica hydrophobic ability in order to afford materials with anticipated functional properties. Improving hydrophobic ability can be achieved by using silylation agent Dimethoxydimethylsilane (DMDMS). Synthesis of hydrophobic silica TEOS-DMDMS was conducted by sol-gel process. TEOS-DMDMS was dissolved into ethanol solution with molar ratio of TEOS:DMDMS:EtOH 1:0.5:50 by using magnetic stirrer. Various acid catalysts (CH\textsubscript{3}COOH, H\textsubscript{2}C\textsubscript{2}O\textsubscript{4}, HNO\textsubscript{3}, and H\textsubscript{2}SO\textsubscript{4}) were added to the ethanol solvent until they reached the same pHs of 3.5. The TEOS-DMDMS sols were used for the surface modification of the glass slide by dip-coating method and then were calcined at temperatures of 300°C, 500°C and 600°C. The hydrophobicity of thin silica thin layers was tested by measuring water contact angle (WCA) and silica xerogels were investigated by TGA and FTIR to determine the thermal properties and characteristics of each functional groups. The WCA values of the uncalcined silica, calcined at 300°C and calcined at 500°C were in the range of 85.4-89.6°, 90.5-92.6°, and 50.4-59.7° respectively. The results of the TGA analysis showed that the TEOS-DMDMS silica began to lose its hydrophobicity starting from temperature of 325°C. The FTIR spectra showed no significant difference in functional groups of the sample prepared from all acid catalysts.

Keywords: DMDMS; hydrophobic; silica films; TEOS

1. Introduction

Synthesis of hydrophobic surface has received much attention in recent years. Hydrophobic surface modification is carried out for various purposes such as in the coating and membrane separation industry [1]. Control the surface properties of the materials, for example by manipulating surface topography and chemical composition is an important way to produce materials with the expected functional characteristic such as anti-fouling [2], anti-icing [3], anti-fogging [4], and self-cleaning [5, 6]. Based on the several methods that are developed in the manufacture of hydrophobic silica thin films, the sol-gel method is the most widely used and most effective method because it has advantages such as producing a higher level of purity, high homogeneity and low temperature in the synthesis process [7].

Some materials commonly used as precursor to synthesis silica nanoparticles are methyltriethoxysilane (MTES), tetraethylorthosilicate (TEOS) and tetramethylorthosilicate (TMOS) which will be modified with hydrophilic or hydrophobic substances [8, 9]. Some researchers use TEOS as a precursor to make a thin layer of silica because TEOS is a source of silica which has a high adsorption performance in the separation of substances, however TEOS is hydrophilic which will be damaged when
interacting with water [10-12]. H$_2$O causes dissociative chemisorption and breakdown of the siloxane structure through hydrolysis reactions because it is susceptible to rehydration through the mechanism of the H$_2$O molecule synthesis in silanol (Si-OH) groups, followed by the reaction with the nearest siloxane [13]. Therefore, it is necessary to change the surface of the silica from hydrophilic to be more hydrophobic by replacing the -OH group of the silica structure with several organic groups through a Si-C covalent bond that cannot be hydrolysed which functions as a matrix modifier [14].

Dimethoxydimethylsilane (DMDMS) contains two hydrophobic methyl groups that can be used as silica precursors [15]. Using of DMDMS to coat a surface will make it more non-polar and more hydrophobic. The silica thin film prepared by TEOS as precursor and DMDMS as co-precursor produced a water contact angle of 165°, while the water contact angle of silica without the addition of silane compounds was around 144°-155° [16]. Research on the hydrophobicity of the thin layer of silica by manipulating various types of acid catalysts (strong and weak acids with varying pH) including HCl, HNO$_3$, HF and HOAc shows that different types of acids affect the gelation time, surface area and pore volume of silica, but have no significant effect on the hydrophobicity of silica [17].

In this research, we developed a study to determine the effect of different types of acid catalysts (strong and weak acids) and heat treatments on the characteristics and hydrophobic properties of silica tetraethoxysilane-dimethoxydimethylsilane (TEOS-DMDMS). The silica xerogels were characterized by TGA and FTIR, while the silica films were examined their hydrophobicity by Water Contact Angle (WCA) measurement.

2. Experimental Study

2.1. Materials.
The materials used in this study were Tetraethylorthosilicate (TEOS) (99% pure) from Merck and Dimethoxydimethylsilane (DMDMS) (98% pure) from Sigma-Aldrich as the silica precursor, ethanol (99.99% pure) from Merck as solvent, HNO$_3$ (65% pure) from Sigma-Aldrich, H$_2$SO$_4$ (95-97% pure) from Merck Millipore, C$_2$H$_5$OH, H$_2$O (≥99% pure) from Sigma-Aldrich, CH$_3$COOH glacial from Sigma-Aldrich, distilled water and glass slide ± 3mm thick.

2.2. Preparation of silica TEOS-DMDMS sols
TEOS-DMDMS solution with various acid catalyst types were synthesized using sol-gel technique by dissolving TEOS-DMDMS into ethanol solvent with molar ratio of TEOS:DMDMS:EtOH = 1:0.5:50 for an hour using a magnetic stirrer. The ethanol solvent pH was previously arranged by adding various acid catalysts (CH$_3$COOH, H$_2$C$_2$O$_6$, HNO$_3$, and H$_2$SO$_4$) until they reached the same pHs of 3.5.

2.3. Preparation of TEOS-DMDMS xerogels
TEOS-DMDMS xerogels were made by pouring TEOS-DMDMS solution into a petri dish to be saved at room temperature for one week, then dried at 60°C in an oven for 2 hours. After drying in the oven, the silica xerogels were calcined in a furnace (Vulcan TM 3-1300) at temperature of 300°C, 500°C and 600°C with a ramp rate of 2°C min$^{-1}$ and steady for an hour.

2.4. Materials Characterization
Uncalcined xerogels were analysed by TGA type STA PT 1600 Linseis with a temperature increase of 5°C/minute to determine the thermal stability in maintaining its hydrophobicity. Furthermore, other xerogels that had been calcined in a furnace (VulcanTM 3-1300) at the temperature of 300°C, 500°C and 600°C were analysed by GSA and Shimadzu Prestige 21 FTIR with techniques KBr pellet for the analysis of the presence of silane groups and the comparison ratio of the group.

2.5. Formation of hydrophobic silica layer
Modification of the glass surface was carried out by dip-coating process where the glass was dipped in TEOS-DMDMS solution by the rate of the dipping and withdrawal was 10 cm/min and 2 minutes’ dwell
time. After that, the coated glass was removed from the TEOS-DMDMS solution and allowed to stand at room temperature to dry, then calcined at 300°C, 500°C and 600°C for one hour in a furnace (VulcanTM 3-1300), with a resistance of 2 hours and a ramp rate of 2°C/min. In order to produce a thicker silica film on the glass surface, the process of silica coating and heat treatment were repeated four times so that no surface cracks occurred.

The hydrophobicity test of the silica layer was conducted by dropping water on the surface of the glass slide that has been coated with TEOS-DMDMS, then photographed it using a camera. Hydrophobic examination of silica films used the 0/2 method to obtain Water Contact Angle (WCA) based on the reported method [18]

3. Results and discussions

3.1. The Measurement of Water Contact Angle (WCA)

WCA measurement was conducted to investigate the hydrophobicity of TEOS-DMDMS silica thin film on the glass surfaces prepared with various acid catalysts and different calcination temperatures. WCA measurement was carried out for the various of acid catalyst types of CH₃COOH, H₂C₂O₄, HNO₃, and H₂SO₄ on uncalcined, calcined at temperature of 300°C and calcined at temperature of 500°C TEOS-DMDMS thin films as shown in Fig. 1.

The picture of water droplets on the glass surfaces in Fig. 1 presents that the TEOS-DMDMS coating on the glass surface increased the hydrophobicity. The water droplet on uncoated glass surface was wide-spread and had low contact angle of 40.2°. While on a coated glass surface, the droplets were more rounded and have larger contact angles. The increase in water contact angle indicates an enhancement in the hydrophobicity of the surface [19]. It could be observed that the presence of TEOS-DMDMS silica layer caused the surface hydrophobicity of the sample increased.

![Figure 1. The photograph showing water droplets on the surface of TEOS-DMDMS silica thin films with various of acid catalysts: (a) CH₃COOH, (b) C₂H₂O₄, (c) HNO₃, and (d) H₂SO₄.](image-url)

The effect of calcination temperature was also observed from the size of water contact angle at temperature of 300 and 500°C. The increase of calcination temperature apparently decreased the water contact angle on the glass surfaces. This was due to calcination at temperatures above 300°C caused the methyl groups were oxidized, then made the surface hydrophobicity to be greatly reduced [20]. These results were supported by the results of TGA and DTG showed in Fig. 3 and Fig. 4. Meanwhile the use
of different acid catalysts in the synthesis of TEOS-DMDMS silica did not give a significant influence on the hydrophobicity of silica.

Fig. 2 depicts the correlation between the WCA values and acid catalyst types used in the synthesis for silica coatings with different calcination temperatures of (a) uncalcined, (b) 300°C and (c) 500°C, respectively. We observed that the thin films prepared with different acid catalysts presented similar water wettability. The WCAs were not significantly different with the acid catalysts used in the synthesis. The contact angle values of the uncalcined TEOS-DMDMS films were in the range of 85.4-89.6°, on the calcination of 300°C were in the range of 90.5-92.6° and on the calcination of 500°C were in the range of 50.4-59.7°. These results indicated that there was a similar interaction between the surfaces with water droplets by this coating. Although not significantly different, there was an interesting point that in silica without calcination and calcination of 300°C, the contact angle increased with increasing acid strength. While the thin layer of silica calcined at a temperature of 500°C showed the opposite, where the contact angle decreased considerably with increasing acid strength of the catalyst used. This was probably due to the release of –CH₃ as a carrier functional group of hydrophobic properties at lower heating temperatures in silica catalysed by strong acids compared to silica catalysed by weak acids. In other words, the silica catalysed by strong acid had a lower thermal stability. This possibility was supported by the data of DTG curve in Fig. 4 that silica catalysed by H₂SO₄ was decomposed faster at lower temperatures compared to other acids.

![Figure 2](image-url)

**Figure 2.** Correlation between the WCA values and acid catalyst types used in the synthesis for silica coatings with different calcination temperatures of (a) uncalcined, (b) 300°C and (c) 500°C.
3.2. Thermal Properties

Thermogravimetry analysis (TGA) was used to characterize materials by measuring the change in mass as a function of temperature and identify the thermal stability of TEOS-DMDMS silica xerogels. The TGA test results are presented in Fig. 3.

The process of weight change of the TEOS-DMDMS silica xerogel in Fig. 3 is occurred into some sections. The first section about 30-125°C called initial drop, the lost weight was due to the loss of ethanol solvents and might other volatile organic substance trapped in the pores of silica xerogel. The average lost weight in this section was small, indicating most ethanol had evaporated while drying at room temperature. The second section at 125-325°C, there was mass reduction signed with a peak at around 200°C of DTG curve in Fig. 4. This mass reduction was caused by an advanced condensation process from Si-OH to form Si-O-Si and releasing H₂O as a by-product, also decomposition of unreacted methyl and methoxy groups from DMDMS precursor. A sharp mass reduction happened at 325-500°C. According to Mahadik et al. [19] the mass reduction in this phase was caused by the decomposition of –CH₃ group oxidized became CO₂. Then, decarbonation process and complete CO₂ release happened due to the decrease in the curve that did not rise again. At the higher temperatures than this, further
oxidation will occur on the methyl groups which are the groups responsible for the hydrophobicity of silica [20].

The DTG curve in Fig. 4 reveals the rate of mass reduction from TGA analysis results. The curve of synthesized TEOS-DMDMS silica xerogels had the differentiation peaks at around 200°C and 400°C. Although the pattern of the DTG curve from silica catalysed by various acids was almost the same, there was a little difference that the silica xerogels catalysed by strong acids, especially by H_2SO_4, was more unstable which was characterized by the peak of differentiation at lower temperatures compared to other acids. This was in line with the results of the WCA measurement which showed that the silica thin layer catalysed using H_2SO_4 had the highest decrease in contact angle.

3.3. Functional Groups Analysis

Fourier Transform Infrared (FTIR) analysis investigated the functional groups and types of silica bonds of TEOS-DMDMS xerogels. Fig. 5 shows the FTIR spectra of silica TEOS-DMDMS without calcination and calcination at temperatures of 300°C, 500°C and 600°C. The striking difference in FTIR spectra was seen at calcination temperatures of 300°C to 500°C. This occurred in all samples with various types of acid. It shows that the difference in the calcination temperature changes the functional groups of the resulting silica xerogels. The peak of Si-C group at the wave number of 840 cm^{-1} and 1257 cm^{-1} obtained from calcination temperature of 300°C was higher than the calcination temperature of 500°C and 600°C. This shows the reduction of Si-C groups in the silica matrix when heated at temperatures above 300°C.

**Figure 5.** TEOS-DMDMS FTIR spectra as a function of different calcination temperature with the acid catalyst used in the synthesis (a) CH_3COOH, (b) C_2H_5O_2, (c) HNO_3, and (d) H_2SO_4.

Calcination at very high temperatures caused the Si-C group to be oxidized to form Si-OH, so that the TEOS-DMDMS spectra without calcination and the calcination temperature of 300°C showed a sharp peak of the wave number for the Si-C groups, while the spectra of the calcination temperature of
500°C and 600°C indicated the peak of the wave number for the Si-C group decreased. The oxidation of Si-C group to Si-OH was supported by the widening of the spectra at wave numbers of 780 cm\(^{-1}\), this was because the presence of hydrogen bonds influenced the shape and intensity of the peak, generally in terms of peak widening or shifting of spectra towards a lower frequency [21]. In addition, the widening of the spectral peak at the wave numbers of 875-750 cm\(^{-1}\) and shifting at the wave number of 1050 cm\(^{-1}\) towards higher wavelengths might be due to the increasing formation of oxides with more formation of CO and the occurrence of structural irregularities caused by heating at very high temperatures [22-24].

The similar pattern shown in Fig. 3, 4 and 5 supported that the use of different acid catalysts did not give a significant effect on the characteristics of the silica produced, indicating that the presence of acid in TEOS-DMDMS silica synthesis worked as a catalyst. This inference needs to be reviewed further by observing the gelation time in silica synthesis as in a study conducted by Pope and Mackenzie [25], which revealed that the presence of acid in silica synthesis acted as a catalyst especially in terms of increasing gelation rate.

**Conclusion**

Silica thin layers were prepared from TEOS-DMDMS sols using various acid catalysts of CH\(_3\)COOH, H\(_2\)C\(_2\)O\(_3\), HNO\(_3\), and H\(_2\)SO\(_4\). The characterization results showed that coating using TEOS-DMDMS sol increased the hydrophobicity of a surface. The Water Contact Angle values of the uncalcined silica, calcined at 300°C and calcined at 500°C were in the range of 85.4-89.6°, 90.5-92.6°, and 50.4-59.7° respectively. The high temperature of calcination affected the hydrophobicity properties associated with the removal of Si-C functional groups responsible for carrying hydrophobic properties. While the TGA and FTIR results of all silica xerogels prepared with different acid catalysts showed almost the same characterization. Using different acid catalysts in the synthesis of TEOS-DMDMS silica sol with the same pH of the solvent did not give a significant influence. However, the silica catalysed by strong acid apparently had lower thermal stability than silica catalysed by weak acid.

**References**

[1] Nady N, Franssen M C, Zuilhof H, Eldin M S M, Boom R and Schroën K 2011 Modification methods for poly (arylsulfone) membranes: A mini-review focusing on surface modification *Desalination* **275** 1-3 1-9
[2] Xie L, Hong F, He C, Ma C, Liu J, Zhang G and Wu C 2011 Coatings with a self-generating hydrogel surface for antifouling *Polymer* **52** 17 3738-44
[3] Liu J, Janjua Z A, Roe M, Xu F, Turnbull B, Choi K-S and Hou X 2016 Super-hydrophobic/icephobic coatings based on silica nanoparticles modified by self-assembled monolayers *Nanomater.* **6** 12 232
[4] Lee H, Alcaraz M L, Rubner M F and Cohen R E 2013 Zwitter-wettability and antifogging coatings with frost-resisting capabilities *Acs. Nano.* **7** 3 2172-85
[5] Meuler A J, Smith J D, Varanasi K K, Mabry J M, McKinley G H and Cohen R E 2010 Relationships between water wettability and ice adhesion *ACS App. Mater. Interfaces* **2** 11 3100-10
[6] Sriramulu D, Reed E L, Annamalai M, Venkatesan T V and Valiyaveettil S 2016 Synthesis and characterization of superhydrophobic, self-cleaning NIR-reflective silica nanoparticles *Sci. Rep.* **6** 35993
[7] Duan Y, Jana S C, Lama B and Espe M P 2016 Hydrophobic silica aerogels by silylation *J. Non Cryst. Solids* **437** 26-33
[8] Darmawan A, Karlina L, Astuti Y, Wang D, Motuzas J and Da Costa J 2017 Interlayer free-nickel doped silica membranes for desalination *IOP Conf. Ser. Mater. Sci. Eng.* **172** 1 012001
[9] Lakshmi R, Bera P, Anandan C and Basu B J 2014 Effect of the size of silica nanoparticles on wettability and surface chemistry of sol–gel superhydrophobic and oleophobic nanocomposite coatings *App. Surf. Sci.* **320** 780-6
[10] Gao Z, Moghaddam S P H, Ghandehari H and Zharov I 2018 Synthesis of water-degradable silica nanoparticles from carbamate-containing bridged silsesquioxane precursor RSC Adv. 8 9 4914-20
[11] Liberman A, Mendez N, Trogler W C and Kummel A C 2014 Synthesis and surface functionalization of silica nanoparticles for nanomedicine Surf. Sci. Rep. 69 2 132-58
[12] Yan H, Yuanhao W and Hongxing Y 2015 TEOS/silane-coupling agent composed double layers structure: A novel super-hydrophilic surface Energy Procedia 75 349-54
[13] Elma M, Yacou C, Wang D K, Smart S and Diniz da Costa J C 2012 Microporous silica based membranes for desalination Water 4 3 629-49
[14] Mhaisagar Y S, Joshi B N and Mahajan A 2012 Surface texture modification of spin-coated SiO2 xerogel thin films by TMCS silylation Bull. Mater. Sci. 35 2 151-5
[15] Rao A P, Rao A V and Pajonk G 2007 Hydrophobic and physical properties of the ambient pressure dried silica aerogels with sodium silicate precursor using various surface modification agents Appl. Surf. Sci. 253 14 6032-40
[16] Nadargi D Y, Kalesh R R and Rao A V 2009 Rapid reduction in gelation time and impregnation of hydrophobic property in the tetraethoxysilane (TEOS) based silica aerogels using NH4F catalyzed single step sol–gel process J. Alloys Compd. 480 2 689-95
[17] Houmard M, Nunes E, Vasconcelos D, Berthomé G, Joud J-C, Langlet M and Vasconcelos W 2014 Correlation between sol–gel reactivity and wettability of silica films deposited on stainless steel App. Surf. Sci. 289 218-23
[18] Darmawan A, Utari R, Saputra R E and Astuti Y 2018 Synthesis and Characterization of Hydrophobic Silica Thin Layer Derived from Methyltrimethoxysilane (MTMS) IOP Conf. Ser. Mater. Sci. Eng. 299 1 012041
[19] Mahadik S A, Mahadik D, Parale V, Wagh P, Gupta S and Rao A V 2012 Recoverable and thermally stable superhydrophobic silica coating J. Solgel Sci. Technol. 62 3 490-4
[20] Tadjarodi A, Haghverdi M, Mohammadi V and Rajabi M 2013 Synthesis and characterization of hydrophobic silica aerogel by two step (acid-base) sol-gel process J. Nanostruct. 3 2 181-9
[21] Sahoo S, Chakraborti C, Behera P and Mishra S 2012 FTIR and Raman spectroscopic investigations of a norfloxacin/carbopol934 polymeric suspension J. Young Pharm. 4 3 138
[22] Ducheyne P 2015 Comprehensive biomaterials vol 1: Elsevier)
[23] Iftiquar S 2002 Structural studies on semiconducting hydrogenated amorphous silicon oxide films High Temperature Material Processes: An International Quarterly of High-Technology Plasma Processes 6 1 40-58
[24] Lung C Y, Heinonen M, Kukk E and Matinlinna J P 2015 Surface modification of titanium with thermally treated polydimethylsiloxane coating and the effect on resin to titanium adhesion Surf. Interface Anal. 47 1 105-12
[25] Pope E J and Mackenzie J 1986 Sol-gel processing of silica: II. The role of the catalyst Journal of Non-Crystalline Solids 87 1-2 185-98