Synthesis and Characterization of Hydrophobic Silica Thin Layer Derived from Methyltrimethoxysilane (MTMS)

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Abstract. This study investigated the synthesis and characterization of MTMS hydrophobic silica prepared by sol-gel method. In principle, silica xerogels and silica thin layer were obtained by reacting MTMS in ethanol solvent in some pH variations. The MTMS solution was used to modify the surface of the ceramic plate by dipcoating method to further be calcined at two different temperatures of 350°C and 500°C. The silica xerogels were analysed by FTIR, TGA-DSC and GSA to determine functional group characteristics, thermal properties and pore morphology respectively. Meanwhile, the silica thin layers were analysed their hydrophobic properties using water contact angle measurement and surface roughness determination using SEM. The results showed that the higher the pH used in the MTMS solution, the higher the resulting contact angle. The highest contact angle was obtained at pH 8.12 which reached 94.7° and 79.5 ° for silica thin layer calcined at 350°C and 500°C, respectively. The TGA results indicated that the methyl group survived up to 400°C and disappeared at 500°C which had implications on silica thin layer hydrophobic nature. GSA result exhibited that the silica xerogel had a close structure with a very low pore volume. While the SEM-EDX results displayed that the silica thin layer prepared at acidic pH had smoother surface morphology and became rough when prepared at an alkaline pH.

Keywords: silica thin layer, hydrophobic silica, methyltrimethoxysilane

1. Introduction
In recent years, silica-based materials have become very attractive because of their unique properties. The magnitude of the possibility to functionalize the silica material, on the surface, the pores and the structure, makes silica applicable to a wide range of applications. The industry's most promising application is the need for thin layers with various structural parameters such as thickness, size and hydrophobicity [1]. Thin layers made from organic silane functioned as precursor were used extensively to modify surfaces hence they had a wide spectrum of applications for example, for coating automotive parts, medical purposes and coating of diagnostic devices. In addition, silane was also commercially available and easy to use [2]. Silane is a substance that can react with an inorganic substrate such as glass or ceramic to form a stable covalent bond thus as to alter the physical interaction of the coated substrate [3].

The various silanes can be used as starting materials for the manufacture of thin silica coatings, some of which are tetraethoxysilane (TEOS) [4], trimethyleoxysilane (TMES) [5], phenyltriethoxysilane (FTES) [6], tetramethoxysilane (TMOS) ) [7], ethyltriethoxysilane (ETOS) [8], trivinyletoxysilane (TVMS) [9], trimethylchlorosilane (TMCS) [10] and hexamethoxydisilane [9]. From various sources of silica precursor, TEOS is the most widely used [11]. Several studies [12-15]
have reported that the use of TEOS resulted in the surface of silica becoming hydrophilic. This indicates that TEOS has a strong hydrophilic character.

On the other hand, the hydrophobic layer is of great concern because of its remarkable nature and has a wide range of potential applications in industry and domestic such as for oil-water separation membranes, anti-dirty surfaces, and coatings on cars [16]. The hydrophobic surface displays a water contact angle greater than 150° consequently it is water resistant. This contact angle is influenced by Si-O-Si, Si-C and C-H functional groups. The more the number of those functional groups, the greater the hydrophobicity properties [17]. To obtain materials that have hydrophobic properties it is necessary to have alternative compounds having larger hydrophobic group contributor.

Methyl trimethoxy silane (MTMS) is a silica precursor having a methyl group which is hydrophobic. Hence, if a surface coated by the MTMS it will be non-polar and more hydrophobic. Several related studies of the hydrophobic silica thin layer of methyl trimethoxy silane (MTMS) have been performed [16, 18-20]. The silica thin layer was prepared by dipcoating method in methanol solvent with volume ratio of MTMS:methanol:oxalic acid:NH$_2$OH of 1: 10: 1: 1 produced a water contact angle of 168° [16]. The aerogel-glass fibres ceramic matrix composite was also successfully produced by sol gel and freeze drying technique using MTMS precursor with superior properties. The composite had a great hydrophobicity and the contact angle up to 131° was achieved [18].

On the other hand, the pH of the sol-gel reaction has been revealed to have considerable influence on the silica polymerization process thus affecting the characters of the resulting silica polymer [21, 22]. The pH affects the hydrolysis and condensation reaction rate, the structure and amount of silica formed. Whilst, the reaction rate of hydrolysis and condensation had the most important effect on the final structure [23]. However, as far as we know, there is no in-depth study of the relationship between pH to silica thin layer hydrophobicity.

In this research, synthesis and characterization of hydrophobic silica thin layer derived from methyl trimethoxysilane (MTMS) through sol-gel process and dip coating were conducted. The effect of pH variation and the calcination temperature on the hydrophobic properties of silica thin layer obtained was assessed using water contact angle measurements, FTIR, TGA-DSC, GSA and SEM-EDX.

2. Experimental Section

2.1. Materials

Materials used were methyl trimethoxy silane (MTMS) 98% Merck Sigma Aldrich (CAS 1185-55-3), ethanol 99.99% Merck Sigma Aldrich (CAS 64-17-5), glacial acetic acid 17.4 M 100% Merck Sigma Aldrich (CAS 64-19-7), ammonia 12.6 M 25% Merck Sigma Aldrich (CAS 7664-41-7), distilled water and a commercial ceramic plate.

2.2. Synthesis and characterization of MTMS xerogel

The MTMS solution was prepared using ethanol solvent with a mole ratio of MTMS: ethanol = 50: 1. Five pH variations were used wherein the ethanol solvent pHs were arranged first by adding acetic acid or ammonia before mixing with the MTMS. The ammonia or acid compositions added are presented in Table 1. Furthermore 3.386 mL of MTMS was added to 70 mL of ethanol solution and stirred using magnetic stirrer for 30 min. The MTMS solution was then dried at room temperature for 2 days, after that the uncalcined xerogels were characterized by the gravimetric analysis performed on a Shimadzu thermo gravimetric analyser TGA-50 using air flow rate of 60 mL min$^{-1}$ and heating rate of 2° C min$^{-1}$. Furthermore, the MTMS xerogels were calcined at 350°C and 500°C for 30 min with a ramp rate of 2°C min$^{-1}$. The MTMS silica xerogels in powder form were characterised using a Shimadzu IRAffinity-1 Fourier-transform infrared (FTIR) spectrometer with a Pike MIRacle attenuated total reflectance accessory (ATR-FTIR) at wavelength range 600-4000 cm$^{-1}$. Samples were degassed under vacuum for more than 6 h at 150 °C before nitrogen adsorption analysis was performed at 77 K and 1 bar using Micromeritic TriStar 3020 instrument. The specific surface area was determined by the Brunauer, Emmett and Teller (BET) method and total pore volume was taken.
from the last point of the isotherm. Average pore diameter (4V/A by BET) was used to determine the average pore sizes.

Table 1. The concentration of acid or base added in ethanol solution

|                      | pH before adding MTMS | pH after the addition of MTMS |
|----------------------|------------------------|-------------------------------|
| 1 M acetic acid in   | 3.44                   | 2.91                          |
| ethanol solution     |                        |                               |
| 0.25 M acetic acid   | 4.52                   | 3.48                          |
| in ethanol solution  |                        |                               |
| 0.025 M acetic acid  | 5.82                   | 4.24                          |
| in ethanol solution  |                        |                               |
| Liquid ethanol       | 8.27                   | 5.49                          |
| without addition of  |                        |                               |
| acid or base         |                        |                               |
| 0.1 M ammonia in     | 9.78                   | 8.12                          |
| ethanol solution     |                        |                               |

2.3. Hydrophobic silica layer formation on glass surface
The ceramic surface modification was carried out by a dipcoating process in which the ceramic was immersed in the MTMS solution by dipping and withdrawal rate of 10 cm min⁻¹ until the entire surface was submerged for 60 seconds. The ceramics were removed from the MTMS solution slowly and dried at room temperature, then calcined at 350°C and 500°C for 30 min at a heating rate of 2°C min⁻¹. The process of dipcoating and calcination was repeated 4 times hence the layer formed was not too thin to prevent the surface rupture. The hydrophobic silica layers formed on the ceramic surface were measured their water contact angle by a water dropping on their surface and then photographed using Samsung Galaxy A5 camera (2016). The 0/2 method is generally used for measurement of contact angle. The contact angle was determined by the equation given below. Where radius r and height h of the droplet.

\[ \tan \theta = \frac{h}{r} \rightarrow \theta = 2 \arctan \left( \frac{h}{r} \right) \]

The contact angle was obtained from the angle of straight lines connecting the left and right ends and the apex of the droplet against a solid surface as shown in Fig. 1.

![Figure 1. Water contact angle measurement](image)

The surface morphology of the ceramic surface was analysed using SEM-EDX 6510 (LA) operated at 20 kV acceleration voltage with dispersive Si (Li) X-ray energy spectrometer. The EDX spectrum was obtained using a JED-2300 system at 20 kV and a distance of 10 mm. The EDX spectra to see the morphology of a thin layer of hydrophobic silica MTMS were analysed by integrated JEOL Analysis Station Software (Version 3.8)

3. Results and Discussion

3.1. The water contact angle on MTMS ceramic plates
The water contact angle analysis aims to determine the hydrophobicity of the MTMS silica thin layer on the ceramic surfaces prepared at different pH and calcination temperatures. On each surface, the water was dropped 3 times on different sides to see the contact angle uniformity on the MTMS silica layer formed. Then the average contact angle was obtained by calculating the average value of three different side water contact angles. Water contact angles at various surfaces are shown in Fig. 2.
Figure 2. The water droplets on the surface of MTMS silica thin films

Figure 2 shows the water droplets on the thin layer of the ceramic surface without MTMS coating and MTMS coated ceramic surfaces prepared at various pHs and calcination temperatures of 350°C and 500°C. It can be seen that the MTMS silica thin layer had a great influence on the surface hydrophobicity. In ceramic without MTMS coating, the water droplets formed were very wide and spread on the ceramic surface, the water contact angle on the ceramic surface was 37°, while after the addition of MTMS, the water droplets were much more rounded which directed the ceramic surface was more hydrophobic. The higher the pH the greater water contact angle whereas the contact angles of the MTMS silica thin films calcined at 350°C were always higher than that of 500°C for all pH variations.

To find the relationship between the contact angles and pH, the a correlation graph was made as presented in Figure 3. Figure 3 presents the relationship between the pH of the MTMS solution to the water contact angles generated by the MTMS silica thin layers, which were calcined at two different calcination temperatures. The higher the pH the greater the contact angle, both on the silica calcined at 350°C or 500°C. The MTMS silica thin layers calcined 350°C had water contact angles greater than that calcined at 500°C since at 500°C the methyl group had been oxidized henceforth the surface hydrophobicity became considerably reduced. These results are supported by the TGA-DSC results presented in Fig. 4 and Fig. 5. According to Mahadik et al [24], the silica layers began losing their hydrophobicity above 550°C and becoming superhydrophilic at 600°C due to the oxidation of methyl groups and other organic groups. According to Budunoglu et al [10], the silica thin layer could retain the hydrophobic properties up to 500°C and at higher temperatures the contact angle decreased and the superhydrophilic layer with contact angle <5° was obtained at a temperature of 600°C. Meanwhile, according to [25], xerogels lost the hydrophobic properties above 325°C, this was due to the fact that at 325°C, the Si-CH₃ group, which was the hydrophobic driving group, underwent oxidation causing the drop of hydrophobicity. Figure 3 has an error margin of 5% and indicates a high linearity in which the regression at 500°C is 0.998 and the regression at 350°C is 0.99. These results reveal that pH is linearly related to the water contact angle.
Figure 3. The relationship between the pH of the MTMS solution and the water contact angles

According to Uhlmann [26], acidic pH generated a long, branched and weak branch of a silica, thereby causing silica thin layer surfaces to become smoother. On the other hands, the alkaline pH resulted in the formation of highly branched and rough silica. The more rough the surface morphology, the higher the surface hydrophobicity of the material [27]. On the hydrophobic surface, surface roughness increases the water contact angle, therefore the surface rises resisting water. Whereas on a hydrophilic surface, the surface becomes softer hence the contact angle decreases and the surface more easily draws water [28]. This explains why the higher (the more alkaline) the pH the greater the contact angle formed.

3.2. Thermal Properties
The analysis of mass changes due to the thermal process was carried out using TGA to identify temperature region at which the dominant weight loss occurred on the MTMS silica xerogel. TGA test results are shown in Fig. 4 and 5.

Figure 4. The mass loss of MTMS silica thin layer at various pHs
Fig. 5. The first derivative of the TGA curves (the DTG curves) at various pHs

Fig. 4 presents a change in the weight of the MTMS silica xerogel as temperature upsurges. Overall, the TGA curves provide the same patterns for the five pH variations with a similar percentage of weight reduction. Fig. 4 and then clarified by Fig. 5 which is the first derivative of the TGA curve display that the process of weight change could be divided into 4 sections i.e. (i) 30°C-125°C, (ii) 125°C-325°C, and (iii) 325°C-550°C (iv) 550°C-800°C. At the section (i) there was a mass reduction caused by the loss of ethanol solvent and other volatile organic materials. The average weight loss was small which less than 2%. This result indicates that most of the ethanol has evaporated during the drying process at room temperature, as well as acetic acid or ammonia. The solvent and organic compound which evaporated in this first section were the solvent and volatile material trapped in the MTMS silica xerogel pores that have not been vanished during the drying at room temperature.

At section (ii) there was a reduction in weight at temperature of 125°C-225°C and characterized by a peak at around 175°C in Fig. 5. This might be due to the further condensation process of the unreacted Si-OH group and formation of the siloxane bond (Si-O-Si) which also released the H2O molecules as the by-product. In this phase, there was shrinkage and compaction of the silica polymers structure. Mass decline may also be due to the decomposition of a small fraction of methyl groups from MTMS and unreacted ethoxy groups. This is in line with [29] which suggested that a weight reduction of the sample heated on air atmosphere at a temperature of 150°C-280°C corresponded to the decomposition of an ethoxy or methoxy group.

In section (iii) there was a sharp mass decline observed at 375-550°C caused by the release of methyl (-CH3) groups from the MTMS xerogel structure because the oxidation reaction formed CO2 (equation 1) and the oxidation of Si-C group became Si-O which further formed a siloxane group. This result is in line with surface hydrophobicity data (Fig. 3) which indicating that the silica thin layer calcined at 500°C had water contact angles which were always lower than that of 350°C. According to Bhagat et. al. [30], this methyl group was responsible for the silica hydrophobicity. The sharp decline in temperature 375-550°C was also accompanied by an exothermic peak on the DSC curve at the same temperature (Fig. 6) due to the decomposition of the -CH3 group and oxidation to CO2 [31].

$$C_xH_y + O_2 \rightarrow CO_2 + H_2O$$

(1)
Figure 6. DSC curves for MTMS silica xerogel at various pH condition

Fig. 6 shows changes in heat flow as temperature increased. At temperatures below 250°C, the curves tend to be flat with slight escalations marked by low and wide peaks at 100°C due to the release of water molecules. This indicated that the silica weight reduction process caused by the solvent evaporation and the following condensation reaction did not release heat. Starting at 250°C there was a sharp rise noticed by an exothermic peak at a temperature of 450°C caused by the oxidation of the methyl group to CO$_2$ and Si-O. After a temperature of 525°C, heat flow continued to rise which might be due to shrinkage continuation of the silica polymer structure even though there was no change in weight occurred at that temperature. Based on the TGA-DSC data, it can be concluded that the MTMS hydrophobic silica xerogels were able to maintain their hydrophobic properties up to 370°C. The calcination above 370°C reduced the hydrophobic properties because the methyl group as a hydrophobic nature guide had been oxidized. However, the incidence of DSC curves for all pH variations indicated that pH gave little effect on the thermal properties of the MTMS silica xerogel.

3.3. Functional group on MTMS silica thin layer
The identification of the bond type and functional group presented in the MTMS silica xerogel was performed by FTIR analysis. The FTIR spectra of the synthesized MTMS silica xerogel are shown in Fig. 7. Fig. 7 confirms that the pH variation and the calcination temperature affected the position, shape and intensity of the MTMS silica xerogel absorbance. The emerging peaks are characteristic for silica polymers located at wave numbers between 1200-750 cm$^{-1}$, i.e. (i) wave numbers of 1150-1000 cm$^{-1}$ indicated the presence of the symmetric and asymmetric vibrations of Si-O-Si [32], (ii) the shoulder region at wave number of 955-835 cm$^{-1}$ in the form of weak absorption overlapping with strong adsorption was attributed to the Si-OH vibration, (iii) the wave number of 865-750 cm$^{-1}$ was assigned to Si-C group which was easily recognized because of the strong and sharp absorption peaks [33], and (iv) a small peak of 1260 cm$^{-1}$ corresponded to the symmetrical vibration of the C-H group [34].
Figure 7. FTIR spectra of MTMS silica xerogel on various pH conditions

According to Mahadik et. al. [31], the difference in calcination temperature resulted in higher Si-OH contents at higher temperatures. The peak intensity associated with -OH increased with temperature step up. At Fig. 7 and the wave number of 955-835 cm\(^{-1}\), the MTMS silica xerogels calcined at 500°C had shoulders higher than that of 350°C. This result implied that the Si-OH group content was higher for silica xerogels calcined at 500°C.

Meanwhile, the intensity of the alkyl group (-CH\(_3\)) decreased after thermal decomposition at a temperature of 352°C, therefore at a calcination temperature of 500°C the peak at the wave number of 865-750 cm\(^{-1}\) was not seen [31]. The MTMS silica xerogel calcined at 350°C had a Si-C peak at 865-750 cm\(^{-1}\) while that of 500°C did not appear at all which indicated that at temperature of 500°C the Si-C group had been much reduced due to high calcination temperature. The same thing happened at the C-H peak at 1260 cm\(^{-1}\) where the peak height was considerably reduced at a temperature of 500°C. The reduced peaks at the wave number of 900 cm\(^{-1}\) appearing on uncalcined silica xerogels, then weakened at calcination temperature of 350°C and completely lost at 500°C were possibly due to burning methyl groups of unreacted MTMS.

For further analysis of the FTIR spectrum, the deconvolution was performed to obtain information about the almost imperceptible differences in the FTIR spectra. In principle, deconvolution develops the experimental spectra into a derived spectrum in which the derived spectra corresponded to the type of functional group to be measured, such as Si-OH, Si-C and Si-O-Si. Quantification of the absorption peaks associated with silanol and siloxane groups may provide an overview of the hydrolysis and
condensation processes in sol-gel reactions [35]. To perform a quantitative analysis, the deconvolution of the peak was used to identify the various vibrations in the overlapping region. All spectra were normalized using the intense peak at 1080 cm$^{-1}$ (Si-O-Si stretching vibration). This peak was baseline resolved and observed to be the least varying peak. Deconvolution of the FTIR spectra was performed using the Fityk software with Gaussian peak during curve fitting. The same number of peaks was used in the entire spectral peak fitting. The half width at half maximum (HWHM) was fixed for each peak, whilst the peak position was allowed to change slightly to realize qualified fitting. Then, the ratios of Si-OH area to Si-O-Si area and Si-C area to Si-O-Si area were calculated to obtain Si-OH/Si-O-Si ratio and C-H/Si-O-Si ratio. The fityk analysis yielded the deconvolution peak of the MTMS spectra as shown in Fig. 8 with the deconvolution peak description shown in Table 2.

![Deconvolution of the FTIR spectra of silica xerogels MTMS at pH 2.91 and calcined at 350°C in the region between 1300 and 900 cm$^{-1}$](image)

**Figure 8.** Deconvolution of the FTIR spectra of silica xerogels MTMS at pH 2.91 and calcined at 350°C in the region between 1300 and 900 cm$^{-1}$

**Table 2.** Description of the deconvolution peaks of the MTMS in Fig. 8

| Deconvolution peak | Wave number (cm$^{-1}$) | Vibrational mode | References |
|--------------------|-------------------------|------------------|------------|
| I                  | 960 cm$^{-1}$           | Si-OH            | [36, 37]   |
| II                 | 1030 cm$^{-1}$          | Linier Si-O-Si   | [38, 39]   |
| III                | 1080 cm$^{-1}$          | Cyclic Si-O-Si   | [39-41]    |
| IV                 | 1150 cm$^{-1}$          | Si-O             | [40]       |
| V                  | ~1220 cm$^{-1}$         | longitudinal optic mode | [38, 39], Si-O-Si |
| VI                 | 1260 cm$^{-1}$          | C-H              | [34]       |

Fig. 9 and 10 present the ratios of peak area between Si-OH/Si-O-Si and C-H/Si-O-Si as functions of pH. Based on Fig. 9, it can be seen that the ratios of the area of Si-OH/Si-O-Si of samples calcined at 350°C were lower than that of 500°C for all pH variations. These results indicated that the relative amount of Si-OH groups on silica calcined at 350°C was less than that of 500°C. On the other hand, the higher the pH, the lower Si-OH/Si-O-Si ratio which may be caused by the Si-OH group binding together and forming the siloxane (Si-O-Si) group. Hydrophobicity is determined by the Si-OH group because Si-OH is easy to interact with water because of the polar OH group [31]. The relatively low Si-OH/Si-O-Si ratio resulted in the interaction between silica thin layer surfaces and water also weak. This result explained why the MTMS silica thin layer calcined at 350°C was more hydrophobic than that of 500°C.
Figure 9. The (Si-OH)/(linier Si-O-Si) ratio for MTMS silica xerogel as function of pH

Fig. 10 shows the C-H/Si-O-Si ratio as a function of pH. The ratio of the area of C-H/Si-O-Si from the silica xerogel calcined at 350°C is higher than that of 500°C for all pH variations. This proved that the relative amount of C-H/Si-O-Si in silica xerogel calcined at 350°C was greater than that of 500°C. The hydrophobic properties are determined by C-H groups derived from methyl groups from MTMS in which the C-H group has weak interaction properties with water [31]. Although, on the silica xerogels calcined at 500°C, the amount of C-H group was considerably reduced because of the oxidation process of the C-H group becoming CO₂. The loss of the C-H group caused the declining of hydrophobic properties of the silica thin layers.

Figure 10. The (C-H)/(linier Si-O-Si) ratio for MTMS silica xerogel as function of pH

3.4. Gas Sorption Analysis

Fig. 11 shows the N₂ adsorption isotherm of the MTMS silica xerogel in which all specified type IV isotherms (as defined by the IUPAC classification), indicating mesoporous network characters. The
MTMS silica xerogel exhibited a low adsorption quantity both in the samples calcined 350°C and 500°C. However, the adsorbed quantities at 350°C were higher than that of 500°C indicating that the higher the calcination temperature, the denser the silica xerogel structure. Apparently, the presence of methyl groups from MTMS had a huge effect on pore structure, since silica xerogel obtained from TMOS (all bonded C binding to methoxy groups) produced large pore volume and surface area [42]. Possibly, the CH₃ group was deposited on the outer surface and inside the cavity thus covering the silica xerogel pores.

![Nitrogen adsorption isotherms of MTMS silica xerogel samples calcined at (a) 350°C and (b) 500°C](image)

**Figure 11.** Nitrogen adsorption isotherms of MTMS silica xerogel samples calcined at (a) 350°C and (b) 500°C

Fig. 12 shows the BET area, pore diameter and pore volume of the MTMS silica xerogel. In general, pore diameter and pore volume was unchange with pH variation even though BET area increased. This results suggested that the increase in pH was related to the BET surface area while the pH had no effect on pore diameter and volume.
Figure 12. BET surface area, average pore size, and average pore volume of MTMS samples calcined at (a) 350 °C and (b) 500 °C

3.5. Morphology and C/O composition (% mass) in MTMS silica thin layer

Analysis of surface morphology and elemental composition of the silica thin layer were performed with SEM-EDX and presented in Fig. 13 and Table 3.

Fig. 13 presents SEM images showing the morphology of two MTMS silica thin layer samples synthesized at the most acidic pH of 2.91 and the most alkaline pH of 8.12. Both were calcined at 350°C with magnification of 500 times. Based on Fig. 12, it can be seen the difference of the resulting silica surface where in the acidic solution which the resulting surface was smoother than that of produced in an alkaline solution. The alkaline pH generated a rougher surface which tended to be more hydrophobic. According to Mahadik et. al. [24], the surface roughness was responsible for the hydrophobic behaviour of the silica layer which reduced the contact of the surface area between the water droplets and the surface of the coating.
Figure 13. The scanning electron microscope (SEM) image of MTMS silica thin layer calcined at 350°C for pH of (a) 2.91 and (b) 8.12

Table 3. EDX results of carbon and oxygen element

| pH  | Element | %Mass | C/O (%Mass) |
|-----|---------|-------|-------------|
| 2.91| C       | 16.19 | 0.30        |
|     | O       | 52.96 |             |
| 8.12| C       | 17.89 | 0.35        |
|     | O       | 51.32 |             |

Table 3 presents the percentage ratio of carbon/oxygen mass obtained from the EDX analysis. It was found that the ratio of carbon to oxygen at pH 2.91 was lower than that of pH 8.12 which were 0.30 and 0.35 respectively. The carbon element tends to be hydrophobic while due to its higher electronegativity, the oxygen element is more hydrophilic. Thus, an upsurge in C/O ratio rose the hydrophobic properties of silica thin layer surfaces [43]. A larger C/O ratio in alkaline pH indicates that at base pH the ceramic surface was more hydrophobic because it contained more carbon than that of acid pH conditions. The high carbon content on the MTMS silica thin layer surface induced the surface became more hydrophobic. A larger C/O ratio at an alkaline pH indicated that under alkaline pH conditions, the silica surface was more hydrophobic because it contained more carbon than the acid pH conditions.

4. Conclusions
A synthesis and characterization study of xerogel and thin silica coatings prepared by MTMS precursors on the surface of the ceramic plate was conducted. The pH greatly influenced the properties of the MTMS silica thin layer, where the higher the pH used in the sol-gel process, the higher the water contact angle which indicated the amplified surface hydrophobicity of silica thin layer. FTIR analysis showed that there was a correlation between the hydrophobic properties of the silica surface and the content of Si-OH and C-H groups. The higher the pH, the lower the Si-OH group as the C-H group increased. The TGA analysis results displayed that the MTMS silica thin layer maintained the hydrophobic properties up to 350°C. The increase in pH was also proportional to the surface area and the roughness of the silica thin layer surface.

Acknowledgments
Adi Darmawan and Yayuk Astuti gratefully acknowledge financial support from Ministry of Research Technology and Higher Education, Republic of Indonesia via the Penelitian Kompetensi (Hikom) with
the grant number of 186-01/UN7.5.1/PG/2016. Adi Darmawan specially thanks for FIM2lab at the University of Queensland for their support for all experimental work.

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