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Effect of Sodium Hydroxide on the Fast Synthesis of Superhydrophobic Powder from Polymethylhydrosiloxane

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Abstract: The paper reports the role of sodium hydroxide in the synthesis of a superhydrophobic powder from polymethylhydrosiloxane (PMHS) in the presence of ethanol and water. The effects of other basic and acidic solutions as well as the absence of water were also investigated. PMHS exhibited rapid gelation (from 8 h to 2 h) by increasing the concentration of sodium hydroxide in the presence of ethanol and water. In contrast, gelation did not occur in the absence of sodium hydroxide or water or in the presence of acidic solutions. Delayed gelation (96 h to 120 h) occurred as a result of the introduction of dipotassium hydrogen phosphate trihydrate. Superhydrophobic powder was obtained by the evaporation of solvents from the gelated sol at 150 °C. The surface properties of the superhydrophobic powder were examined by scanning electron microscopy, high resolution transmission electron microscopy, N_2 sorption isotherm, and X-ray diffraction. The particle size, functional groups and thermal stability of the powder were analyzed by dynamic light scattering spectroscopy, Fourier transform infrared spectroscopy, ^{29}Si cross polarization magic angle spinning nuclear magnetic resonance spectroscopy, and thermogravimetric analysis. The surface properties of the powder were also assessed by contact angle measurements. The results showed that increasing the concentration of sodium hydroxide added to PMHS or increasing the drying temperature of the gelated sol resulted in the more rapid formation of superhydrophobic powder.

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1. INTRODUCTION

The wettability of a solid surface is defined by its ability to be wetted or dewetted by the contact of a liquid water droplet. Based on the wettability phenomena, the surface properties of a solid substrate can be classified as superhydrophilic, hydrophilic, hydrophobic and superhydrophobic according to their contact angles (CAs) [1]. A substrate surface with very low CA (<5°) is defined as a superhydrophilic surface. A substrate surface with CA less than 90°, and 90° to 150° and greater than 150° are defined as hydrophilic, hydrophobic and superhydrophobic or self-cleaning surfaces, respectively [1-3]. Over the recent decade, superhydrophobic surfaces have found many applications, such as the adsorption and separation of oils from water, cultivation of micro-organisms, photocatalysis, anti-reflective coating, moisture resistant surfaces, sensors, and other applications, because of their non-stick and self-cleaning properties [4-8]. Superhydrophobic powders have recently begun to play a vital role in several applications, such as the formation of liquid marbles, superhydrophobic magnetic particles and bio-medical applications [9-12]. These types of superhydrophobic surfaces and materials are prepared using several methods, such as top-down, bottom-up and combinations of top-down and bottom-up approaches [4, 13]. A wide range of superhydrophobic surfaces have been prepared using these approaches and some have been commercialized.

Several factors were considered when synthesizing superhydrophobic materials or fabricating superhydrophobic surfaces based on the above methods. Recently, sol-gel method has attracted considerable attentions for the superhydrophobic surface fabrication. This is mainly due to the simple synthesis of superhydrophobic material by hydroxylation and condensation of silane precursors and easy fabrication of superhydrophobic surface by various coating methods such as dip coating, spin coating, casting, spraying, and drop coating, etc. Meanwhile, optimization of the material by sol-gel method is the most important criteria to fabricate uniform surface phenomena. The optimization of sol-gel methods depends on the kinds of silane precursors, catalyst, stirring time, rotation speed, reaction conditions (temperature, oil or water bath), and drying temperature etc. [14]. In this work, superhydrophobic powder was synthesized by self-hydroxylation and condensation of polymethylhydrosiloxane (PMHS) using sodium hydroxide solutions ($NaOH/H_2O$) as a catalyst in the presence of ethanol by referring to previous studies [5, 15].

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Table 1: Synthesis of Superhydrophobic Powders under Various Concentrations of Catalysts

Sample Name	PMHS (g)	Ethanol (mL)	NaOH (g)	$K_2HPO_4.3H_2O$ (g)	Aq. Ammonia (mL)	HCl (mL)	H_2O (mL)	Gelation Time (hr)
PS1	4.7	70	0.008	-	-	-	2	8
PS2	4.7	70	0.016	-	-	-	2	6
PS3	4.7	70	0.024	-	-	-	2	5
PS4	4.7	70	0.032	-	-	-	2	3
PS5	4.7	70	0.04	-	-	-	2	2
PK1	4.7	70	-	0.05	-	-	2	96-120
PK3	4.7	70	-	0.14	-	-	2	96-120
PK5	4.7	70	-	0.23	-	-	2	96-120
PA1	4.7	70	-		0.12	-	9.88	-
PA2	4.7	70	-		0.24	-	9.76	-
PA3	4.7	70	-		0.36	-	9.64	-
PH1	4.7	70	-		-	0.1	9.90	-
PH2	4.7	70	-		-	0.2	9.80	-
PH3	4.7	70	-		-	0.3	9.70	-

*S, K, A and H represent the presence of NaOH, $K_2HPO_4.3H_2O$, aqueous ammonia and HCl, respectively.

PMHS is a siloxane-based transparent liquid with potential use in a wide range of applications owing to its high thermal stability, inertness to air and moisture, solubility in common organic solvents, hydrophobicity, and low surface energy [16-18]. Some uses of PMHS include superhydrophobic materials, catalysis, preparation of highly transparent and anti-stain substrates, liquid crystalline polymers (LCPs), ceramics, and the formation of nano necklaces [5, 9, 15, 19-23]. Despite of several advantages of PMHS, to the best of authors' knowledge, the use of PMHS for the synthesis of superhydrophobic materials and their uses for practical applications were limited [5, 24, 25]. Yang *et al*. synthesized superhydrophobic powder by using PMHS and tetraethoxysilane (TEOS) in the presence of NaOH/water and ethanol [9]. They checked the adsorption behaviour of superhydrophobic powder for the adsorption of traces of alkylphenols in water [25]. Zhai *et al*. also prepared a similar type of superhydrophobic mesoporous xerogel powder using PMHS and bridged bis-(triethoxysilyl)etane (BTME) in the presence of NaOH/water and ethanol [26]. The superhydrophobic powders were obtained with the total time of 3-5 days [9, 25, 26]. Our previous study also showed that it took almost 2-3 days to synthesize polymethylhydroxysiloxane (PMHOS) powder even by one-pot approach [5]. The effect of catalysts and the effect of drying temperature were not discussed elsewhere for the PMHS under self-hydroxylation and condensation. Due to the excellent thermal stability of the superhydrophobic powder, increasing the drying temperature would reduce the material synthesis time. Based on the above concepts, we examined the effects of sodium hydroxide solutions for the rapid synthesis of superhydrophobic powder from PMHS [5, 15]. Increasing the concentration of NaOH to PMHS led to faster the gelation time from 8 h to 2 h. In this work, solvents were evaporated after the complete condensation of PMHOS by keeping the self-hydrolyzed and condensed sol for 24 h of total reaction time. On the other hand, the drying temperature was increased from 80 °C to 150 °C and the drying time was reduced from 24-30 h to 2-4 h. Hence, the changes in the surface properties of a superhydrophobic powder by increasing the concentration of a sodium hydroxide solution or by increasing the drying temperature to 150 °C were investigated in this work. The main advantage of the study illustrates the faster synthesis of superhydrophobic powder by the increase of catalyst concentrations and drying temperature over other processes reported elsewhere. Moreover, the superhydrophobic powder can also be prepared rapidly by the evaporation of solvent after the complete gelation (2 h or 8 h). The effects of other basic and acidic solutions for the synthesis were also checked based on the experimental procedure.

2. EXPERIMENTAL DETAILS

2.1. Materials

PMHS (Mn ~1700 to 3200) and dipotassium hydrogen phosphate trihydrate ($K_2HPO_4.3H_2O$) were acquired from Sigma-Aldrich. Anhydrous ethanol (special grade) was obtained from Carlo Erba Reagents Co. Ltd. Sodium hydroxide (NaOH) and ammonia solution (NH_3, 28-30% (m/m)) were purchased from Junsei Chemical Co. Ltd.

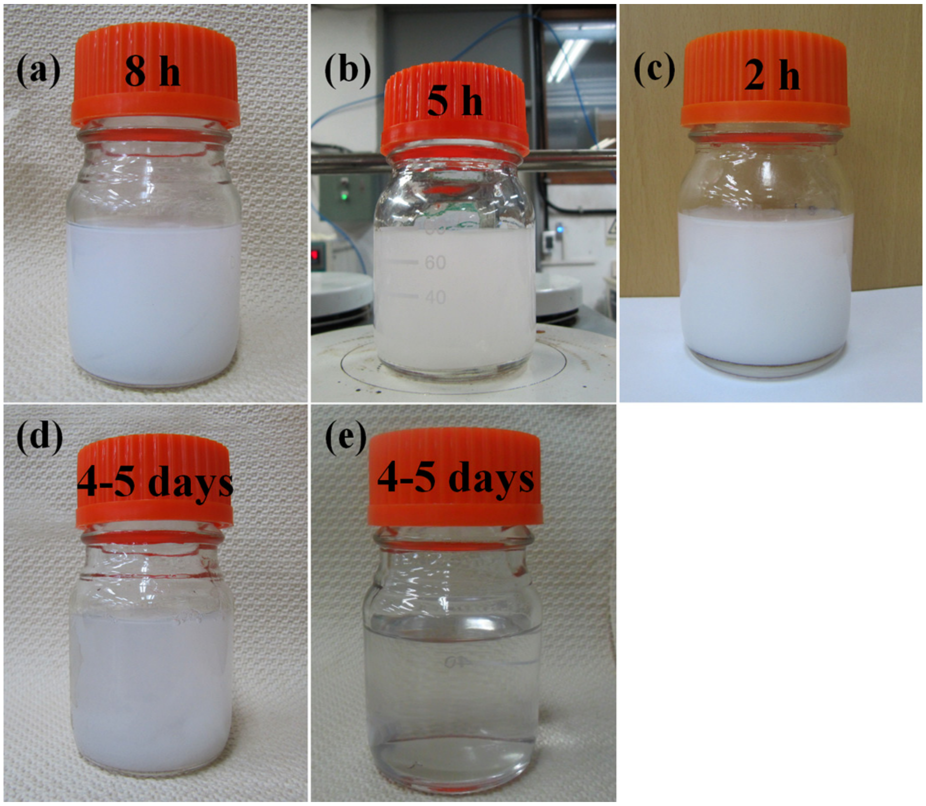

Figure 1: Optical images of PMHS after adding various concentrations of NaOH (PS1 (**a**), PS3 (**b**) and PS5 (**c**)), $K_2HPO_4.3H_2O$ (PK5 (**d**)) and HCl (PH1 (**e**)) in ethanol/water medium.

Hydrochloric acid (HCl) (Guaranteed reagents) was supplied by Matsunoen Chemicals Ltd. Double deionized water was used in all experiments.

2.2. One-Spot Synthesis of Superhydrophobic Polymethylhydroxysiloxane

PMHS (4.7 g, 78 mmol MeHSiO) was dissolved in anhydrous ethanol (70 mL) in a 100 mL glass container and hydrolyzed by the addition of a sodium hydroxide (0.2 mmol in 2mL of water) solution [5, 15]. The hydrolyzed sol was gelated in 8 h and stirred further for a total stirring time of 24 h (Figure **1** and Table **1**). The gel was condensed further and dried at 150 °C for 2 h. The superhydrophobic product was ground to a powder, washed several times in deionized water and dried for a further 2 h at 150 °C, followed grinding to a fine powder. The experiment was repeated with various NaOH ratios (0.4 mmol, 0.6 mmol, 0.8 mmol and 1.0 mmol) or $K_2HPO_4.3H_2O$ (0.2 mmol, 0.5 mmol and 1.0 mmol) or with aqueous ammonia (0.1 M, 0.3 M and 0.5 M, 2 mL of 10 mL of ammonia/water solution) and HCl (0.1 M, 0.3 M and 0.5 M, 2 mL of 10 mL of HCl/water solution) solutions (Table **1**). The gelation of sol became faster from 8 to 2 h by increasing the concentration of NaOH (0.4 mmol (6 h), 0.6 mmol (5 h), 0.8 mmol (3 h), and 1.0 mmol (2h)). The gel was condensed further to form complete siloxane networks with the total time of 24 h and then dried at 150 °C based on the experimental procedure and repeated washing and drying processes. The experiment was also repeated in the absence of NaOH and water. Table **1** provides more details on the synthesis of superhydrophobic powders. The synthesized superhydrophobic powder is referred to as PMHOS or P. The synthesized powder is also called PS1-PS5, PK1, PK3, PK5, PA1-PA3, and PH1-PH3, based on the concentrations of the basic and acidic solutions, where S, K, A and H indicate the presence of NaOH, $K_2HPO_4.3H_2O$, aqueous ammonia, and HCl, respectively.

2.3. Characterization

The surface morphology of the superhydrophobic powder was examined by scanning electron microscopy (SEM, Table-top Mini, SNE-3000M). The samples were placed on a carbon tape and coated with gold before the measurements. The material surface was also examined by high resolution transmission electron microscopy (HR-TEM, JEM 2011 at 200 kV). PMHOS was dispersed well by ultra sonication for 60 min. in ethanol and collected on a copper grid before the measurement. The particle surface area, pore volume and pore diameter were measured by a Micromeritics ASAP 2020 V3.04 G surface area and pore size analyzer, and calculated using the Brunauer–Emmett–Teller (BET) method and Barrett–Joyner–Halenda (BJH) analysis [27]. The structural properties of the particles were analyzed by X-ray diffraction (XRD) using a Miniflex goniometer at a scanning range from 1.2°-80° 2θ. Dynamic light scattering (DLS, Zeta sizer, Nano S90) was used to measure the particle size of the samples. Before the measurements, the superhydrophobic powder was dispersed well in ethanol for 24 h. The functional groups present in the superhydrophobic powder were analyzed by Fourier transform infrared (FTIR, JASCO (FTIR-4100)) spectroscopy and ^{29}Si cross polarization magic angle spinning nuclear magnetic resonance (^{29}Si CP MAS NMR) spectroscopy using a 400 MHz Avance II+ Bruker Solid-state NMR at the Korea Basic Science Institute (KBSI) Daegu Centre. The thermal stability of the superhydrophobic powder was estimated by thermogravimetric analysis (TGA, Q50 V6.2, Build 187, TA instruments, U.S) in a nitrogen atmosphere at a heating rate at 10 °C/min. The superhydrophobic powder dispersed in ethanol was coated on a glass substrate and the surface properties of the coated powder were examined by contact angle (CA) measurements using a drop shape analysis system (DSA 100, Krüss GmbH, Germany)). The measurements were carried out in 500 µL syringe with a needle, 0.5 mm in diameter and 38 mm in length with a liquid volume of 8 µL under a flow rate of 600 rpm [28].

3. RESULTS AND DISCUSSION

A previous study revealed the gelation of PMHS in the presence of NaOH in ethanol/water medium. The PMHOS powder (in NaOH (0.2 mmol) at 80 °C) obtained from the gel showed a micro-nano hierarchical surface morphology with superhydrophobicity [5]. The results in the current study revealed the effect of NaOH and water on the gelation of PMHS through self hydroxylation and condensation. The hydrolysis and condensation of PMHS by the addition of NaOH in ethanol medium would deliver the exchange of ethoxy and hydroxy groups with the highly reactive Si-H groups in PMHS [9]. Under this condition, PMHOS forms a helical structure with hydrophobic methyl and hydrophilic hydroxy groups at the inner and outer loop of the material surface. Further condensation occurred in the siloxane chains through the evaporation of the solvents from the sol at 150 °C for 2 h, which leads to the production of stronger hydrophobic methyl groups on the surface. The superhydrophobic property was obtained by washing the sample in an excess of water and dried again at 150 °C for 2 h [5, 9, 15]. Increasing the NaOH concentration (from 0.2 mmol to 1 mmol) to the PMHS accelerated gelation from 8 h to 2 h (Figure **1a-c**). Similarly, increasing the drying temperature of the gelated sol from 80 °C to 150 °C reduced the synthesis time of the superhydrophobic powder from 2-3 days to 1-2 days. On the other hand, gelation did not occur in the absence of NaOH or water. The effects of NaOH over other basic and acidic solutions on the synthesis of the superhydrophobic powder were examined (Table **1**). The addition of $K_2HPO_4.3H_2O$ (in ethanol and water) can allow the slow formation of a sol, followed by gelation in 96-120 h. PMHS could not form a sol or gel in the presence of aqueous ammonia or HCl. The results clearly show that NaOH plays a major role in the sol-gel behavior and accelerate the gelation of PMHS over other basic and acidic solutions.

Figure **2** shows the surface morphology of PMHOS synthesized from various NaOH and $K_2HPO_4.3H_2O$ concentrations. PS1 showed similar micro-nano hierarchical surface properties and superhydrophobicity to those obtained at 80 °C in a previous study (Figure **2a**) [5]. The surface properties were altered partially by increasing the NaOH concentration (Figure **2a-e**). On the micro scale, the PS1-PS5 samples showed a flake-like morphology of layered networks of siloxane chains (Figure **2a-e**). The layered networks of the siloxane chains increased with increasing NaOH concentration (Figure **2**). A flake-like morphology was also obtained for the material prepared using $K_2HPO_4.3H_2O$ (PK5) (Figure **2f**). The SEM images illustrate the formation of hierarchical surface morphology of the micro-nanoparticles of PMHOS. This hierarchical micro-nano surface morphology

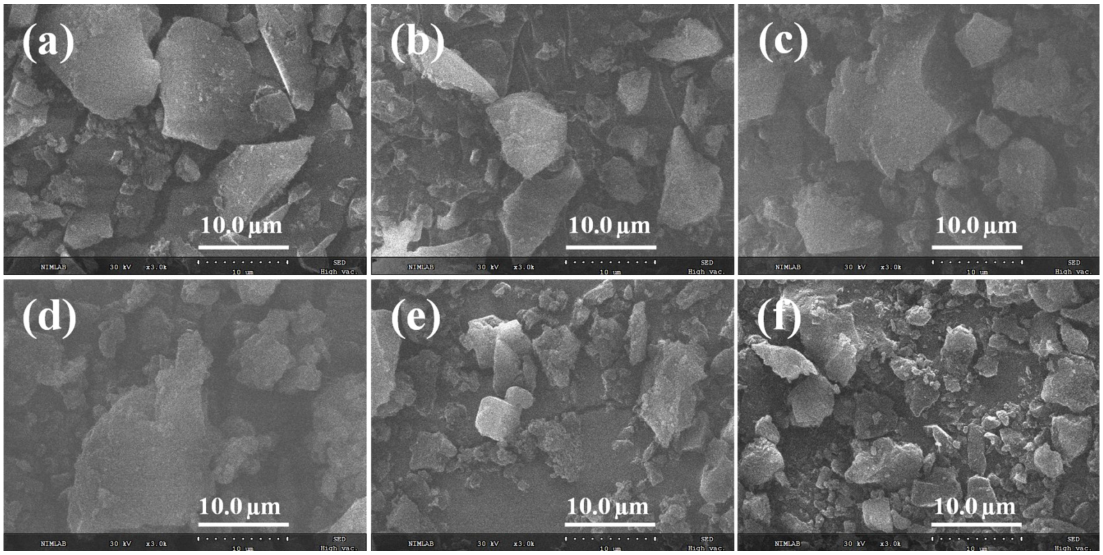

Figure 2: SEM images of the synthesized superhydrophobic powder obtained with various concentrations of NaOH ((**a**) PS1, (**b**) PS2, (**c**) PS3, (**d**) PS4, (**e**) PS5), and $K_2HPO_4.3H_2O$ ((**f**) PK5).

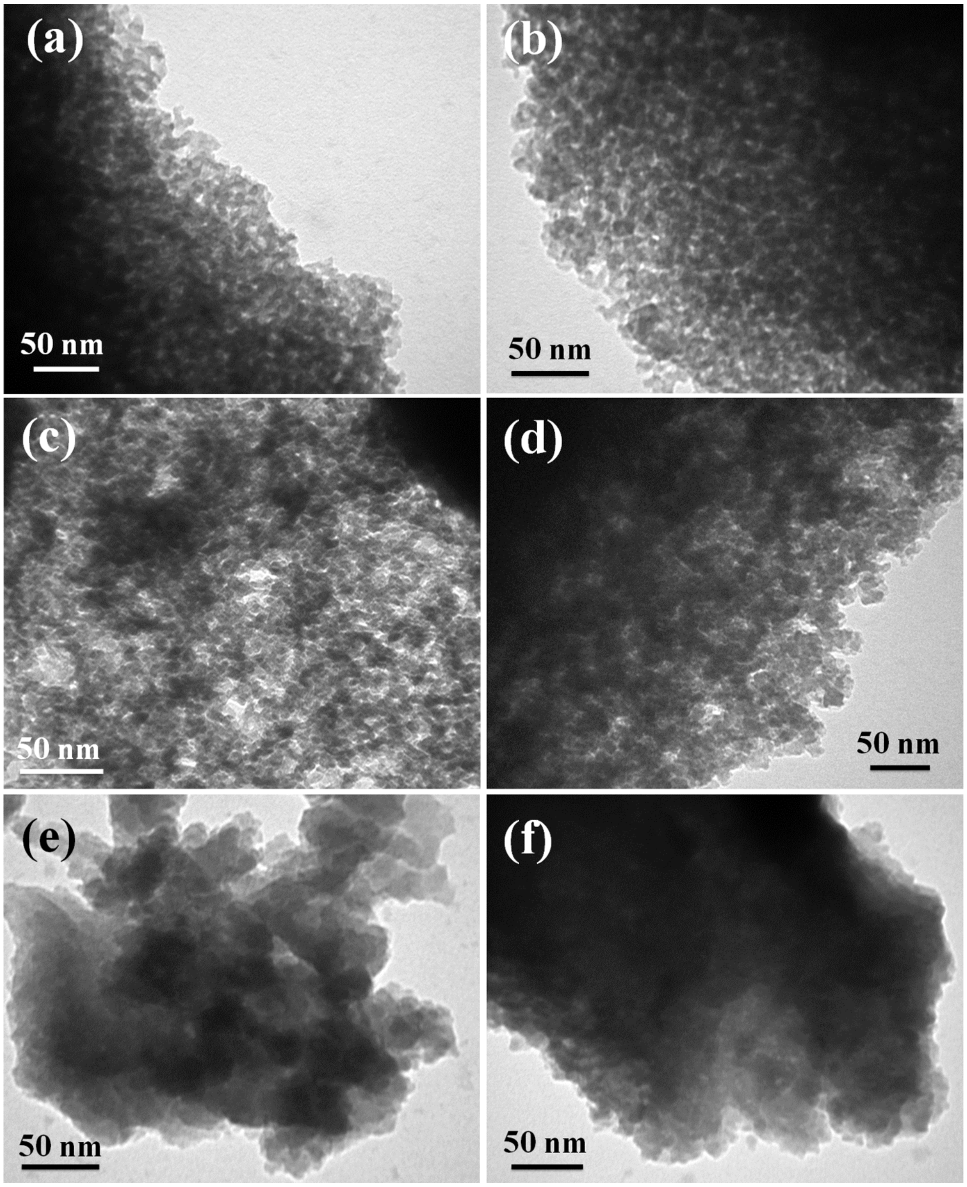

Figure 3: HR-TEM images of the synthesized superhydrophobic powder obtained with various concentrations of NaOH ((**a**) PS1, (**b**) PS2, (**c**) PS3, (**d**) PS4, (**e**) PS5), and $K_2HPO_4.3H_2O$ ((**f**) PK5).

with hydrophobic methyl groups anchored on the surface would maintain the stable superhydrophobicity of the material surface when coating the dispersed suspension on a glass substrate. The HRTEM images of the PS1-PS5 samples revealed a porous structure of the hierarchical micro-nanoparticle (Figure **3a-e**). The porous structure of the material was mainly due to the formation of siloxane networks of the PMHS under self hydroxylation and condensation. On the other hand, the porous structure of the material was changed significantly by increasing the NaOH concentration as well as curing the gel at 150 °C [5]. The changes in the morphology of the samples were attributed to the faster gelation of the material. Increasing the concentration of NaOH from 0.2 mmol to 0.4 mmol and 0.6 mmol, the surface area and pore diameter were increased. The HRTEM images of PMHOS prepared with 0.4 mmol and 0.6 mmol of NaOH also showed the enhanced porous morphologies of the samples (Figure **3a-c**). This could be confirmed further by BET sorption analysis. The porous structure of the materials was reduced by further increasing the concentration of NaOH from 0.6 mmol to 1 mmol. The results indicated that the addition of up to 0.6 mmol (PS3) of NaOH in 2 mL H_2O would be a sufficient amount for the synthesis of superhydrophobic powder. The change in surface morphology was also obtained when higher $K_2HPO_4.3H_2O$ concentrations were used (PK5) (Figure **3f**). The porous structure of PMHOS was reduced by the addition of $K_2HPO_4.3H_2O$ solution instead of NaOH solution. The obtained surface of the material showed thick layers of the siloxane networks of the material (Figure **3f**). The DLS spectra indicated a change in the particle size by the increase in NaOH concentration. At lower NaOH concentrations (PS1), the spectrum revealed a dual (micro and nano) particle size (Figure **4A**, Table **2**). The main cause of such a dual particle size might the complexity arising from the difference in the rate of particle gelation as well as the self-hydrolysis and condensation rates of PMHS, depending on the concentration of either NaOH or $K_2HPO_4.3H_2O$. On the other hand, the mean particle size of the sample increased with increasing NaOH concentration [29, 30]. At higher NaOH concentrations (PS5), the particle size of the superhydrophobic powder increased to a micrometer size (Figure **4A**, Table **2**). A higher NaOH concentration and faster gelation of the siloxane backbone might increase the particle size of the final material, whereas increasing the concentration of NaOH might twist the hydrophobic and hydrophilic substitutions in the cross-linked siloxane chain towards the surface *via* a hydroxylation and condensation reaction. At higher NaOH concentrations, PMHS favors the formation of hydrophilic groups on the PMHOS surface, which is due to electrostatic attractions between PMHOS and NaOH and the possibilities of exchanging the ethoxy groups in ethanol. On the other hand, the strongly hydrophobic methyl groups maintain the hydrophobicity of the material. Superhydrophobicity was obtained by washing the sample in an excess of water followed by drying at 150 °C. During the gelation and co-condensation stage, the surface properties of the material were changed significantly and the particle size increased. In contrast, the dual micro-nano particle sizes of the samples were reduced by increasing the concentration of $K_2HPO_4.3H_2O$ added to the PMHS (Figure **4** and Table **2**). These conflicting properties were attributed mainly to the gelation effect of NaOH and $K_2HPO_4.3H_2O$ with PMHS. NaOH is more favorable and easily hydrolyzed the PMHS in ethanol/water medium than $K_2HPO_4.3H_2O$.

Figure **5** shows XRD patterns of PMHOS synthesized using various concentrations of NaOH. PMHOS showed two important peaks (sharp and broad) at 9.36° 2θ (003 plane) and at 16.11 to 30.50° 2θ, indicating the crystalline and amorphous peaks of alkyl chain present at the siloxane backbone, respectively [5]. The sharp peak at 9.36° 2θ shifted towards a higher angle 10.51° 2θ and became identical by increasing the NaOH concentration. The obtained results suggest that a significant change in the superhydrophobic material by increasing the concentration of NaOH. Figure **6** shows the N_2 adsorption and desorption isotherms, pore volumes and pore size distributions of the synthesized superhydrophobic PMHOS. The superhydrophobic powder showed a H_2 hysteresis loop with a type IV isotherm peak, indicating the disordered mesoporous structure of PMHOS [22]. A previous study also revealed the disordered mesoporous structure of PMHOS synthesized at a

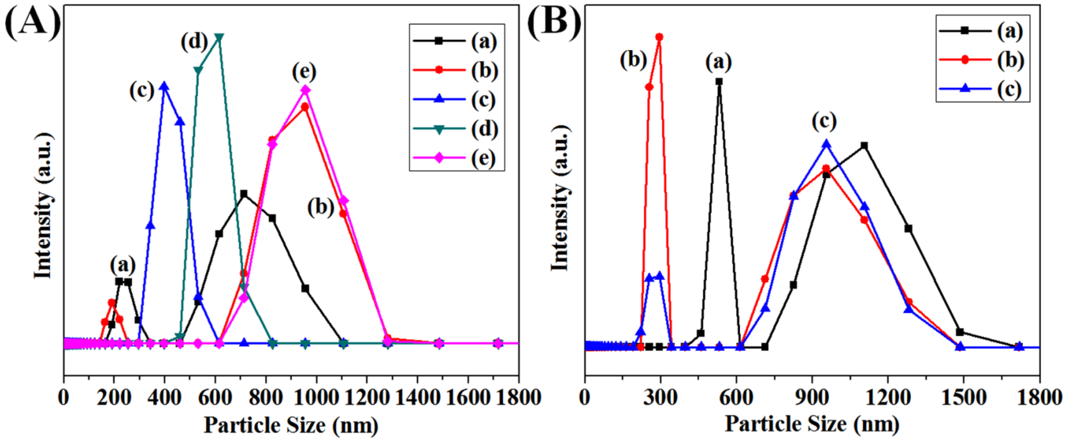

Figure 4: DLS particle size spectra of the synthesized superhydrophobic powder obtained with various concentrations of NaOH ((**A**) PS1 (**a**), PS2 (**b**), PS3 (**c**), PS4 (**d**) and PS5 (**e**)), and $K_2HPO_4.3H_2O$ ((**B**) PK1 (**a**), PK3 (**b**) and PK5 (**c**)).

Table 2: **DLS Particle Size Data of Superhydrophobic Powder Obtained at Various Concentrations of NaOH and $K_2HPO_4.3H_2O$**

Sample Name	Dual Particle Size	
	Micro Particle Size (nm)	**Nano Particle Size (nm)**
PS1	731	240
PS2	957	192
PS3	-	397
PS4	609	-
PS5	957	-
PK1	1104	534
PK3	957	292
PK5	957	270

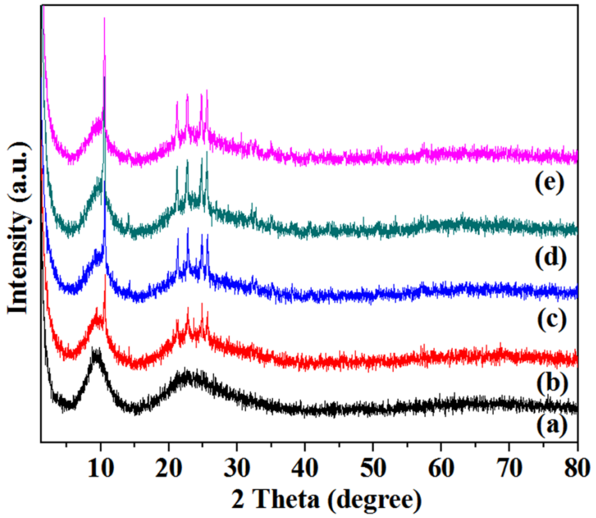

Figure 5: XRD patterns of the synthesized superhydrophobic powder obtained with various concentrations of NaOH ((**a**) PS1, (**b**) PS2, (**c**) PS3, (**d**) PS4 and (**e**) PS5).

drying temperature of 80 °C with a surface area, pore volume and pore diameter of 413 m^2/g, 1.08 cm^3/g and 25.1 nm, respectively [5]. On the other hand, the surface area (334 m^2/g), pore volume (0.33 cm^3/g) and pore diameter (5.5 nm) were lower when the drying temperature of the gelated sol was higher (see Table **3**). Increasing the concentration of NaOH added to the PMHS showed an increasing trend in the surface area, pore volume and pore diameter of the samples, even though the trend in the surface area was not consistent. HRTEM images also agreed with the change in surface properties of the superhydrophobic powder by increasing the concentration of NaOH (Figure **3**). The results showed that both the NaOH concentration and drying temperature play key roles in controlling the surface area, pore volume and pore diameter, but the precise mechanism is unclear.

FTIR spectroscopy showed the important peaks of PMHS, such as Si-H, Si-O-Si and Si-CH_3 at 2170 cm^{-1}, 1030-1130 cm^{-1} and 1260 cm^{-1} (Figure **7a**), respectively [20, 21]. The disappearance of a Si-H peak at 2170 cm^{-1} and the splitting of the Si-O-Si peaks to 1037 cm^{-1} and 1122 cm^{-1} confirmed the self-hydroxylation and condensation of PMHS under NaOH (Figure **7b**) [5]. Si-OH peaks were observed at 3437 cm^{-1} and 910 cm^{-1} and Si-CH_3 peaks were noted at 2973 cm^{-1}, 2916 cm^{-1}, 1273 cm^{-1}, 847 cm^{-1}, and 777 cm^{-1}. The results suggest that the addition of NaOH cause a significant change in the functional groups (Figure **7a** and **b**). On the other hand, increasing the NaOH concentration also showed similar peaks to those obtained at the initial NaOH concentration (Figure **7b-f**). ^{29}Si-NMR spectroscopy also confirmed the above concept of similar functional groups (T^3 (-59.6 ppm), T^2 (-55.9 ppm) and M^1 (8.14 ppm)) after increasing the NaOH concentration or by the addition of $K_2HPO_4.3H_2O$ (Figure **8**) [5]. A peak at -20.7 ppm in PS1 might be due to the presence of impurities and the noise peak of the sample. On the other

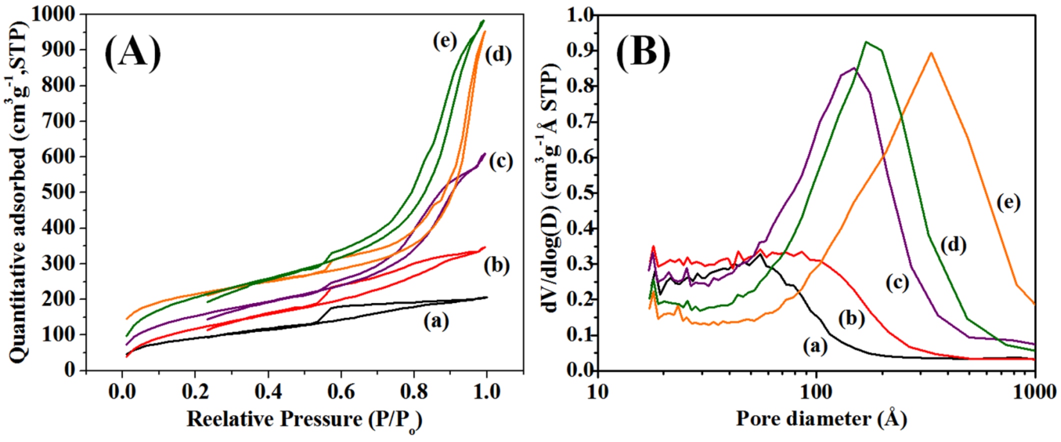

Figure 6: ((**A**) and (**B**)) N_2 adsorption and desorption isotherms and pore size distributions curves of the synthesized superhydrophobic powder obtained with various concentrations of NaOH ((**a**) PS1, (**b**) PS2, (**c**) PS3, (**d**) PS4, and (**e**) PS5).

Table 3: BET Surface Areas and Pore Size Distributions of the Superhydrophobic Powders Prepared at Various Concentrations of NaOH

Sample	BET surface Area ($m^2 g^{-1}$)	Total pore Volume ($cm^3 g^{-1}$)	BJH pore Diameter (nm)
PS1	334	0.33	5.5
PS2	432	0.45	8.6
PS3	459	0.75	15.0
PS4	296	0.81	18.2
PS5	371	0.74	33.2

hand, the well known Si-H (D_2H, -34.7 ppm) peak disappeared by self-hydroxylation and condensation of PMHS in the presence of NaOH or $K_2HPO_4.3H_2O$ in water and ethanol [5, 9, 31, 32]. The M^1, T^2 and T^3 peaks of PS1, PS3 and PS5 confirmed the cross linked networks of the siloxane chain. Significant changes in the peak intensity of T^2 at -55.9 ppm were observed after increasing the NaOH concentration. These changes would not affect the functional groups present in the superhydrophobic powder. A similar spectrum was also observed for the sample prepared from $K_2HPO_4.3H_2O$ (PS5). The results suggest that an increase in the NaOH or $K_2HPO_4.3H_2O$ concentration added to PMHS might alter the surface properties and particle size rather than the functional groups present in the material.

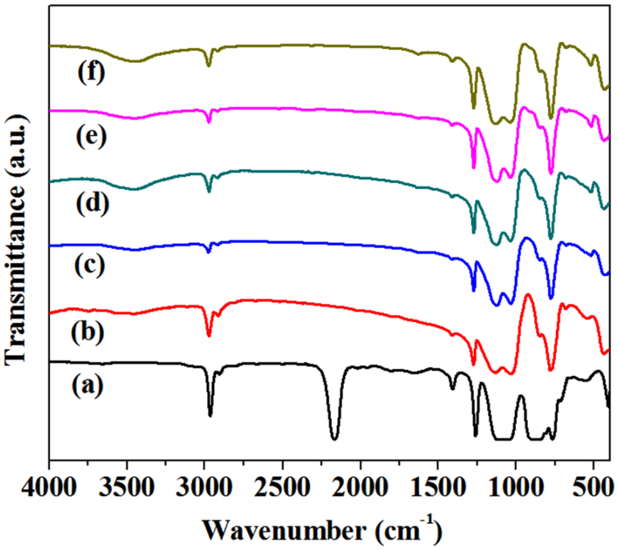

Figure 7: FTIR spectra of the synthesized superhydrophobic powder obtained with various concentrations of NaOH ((**a**) PMHS, (**b**) PS1, (**c**) PS2, (**d**) PS3, (**e**) PS4, and (**f**) PS5).

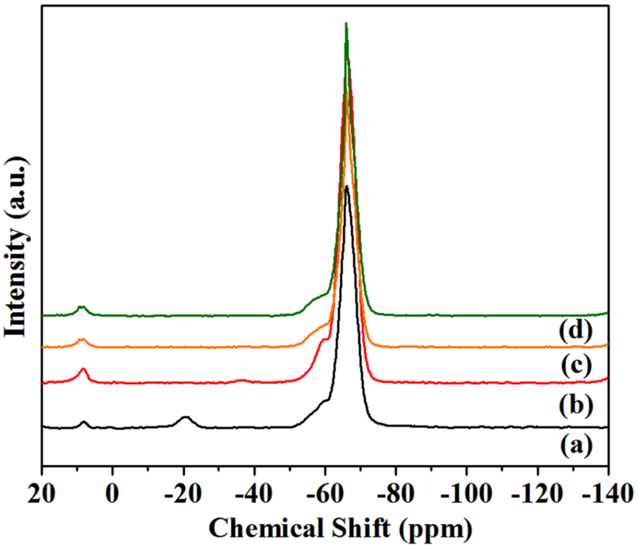

Figure 8: ^{29}Si-CP-MAS NMR spectra of the synthesized superhydrophobic powder obtained with various concentrations of NaOH ((**a**) PS1, (**b**) PS3, (**c**) PS5), and $K_2HPO_4 \cdot 3H_2O$ ((**d**) PK5).

Figure **9** shows the TGA curves of the PS1-PS5 samples. The strong organic group [MeSiO] present in PMHS might show very good thermal stability over a range of applications. The hydroxylation and polycondensation of PMHS might further enhance the thermal stability of the material due to the presence of methyl functional groups at the cross linked network of the siloxane backbone [9, 33]. PS1 revealed an initial decomposition temperature of ~325 °C (Figure **9a**). This good thermal stability was attributed mainly to the network structure of the superhydrophobic powder. On the other hand, the organic moiety decomposed at a high decomposition temperature. The maximum decomposition of PS1 occurred at ~445 °C (Figure **9a**). The material looses the organic moieties beyond this temperature with complete removal observed at more than 605 °C. At that stage, the superhydrophobic powder became superhydrophilic [5].

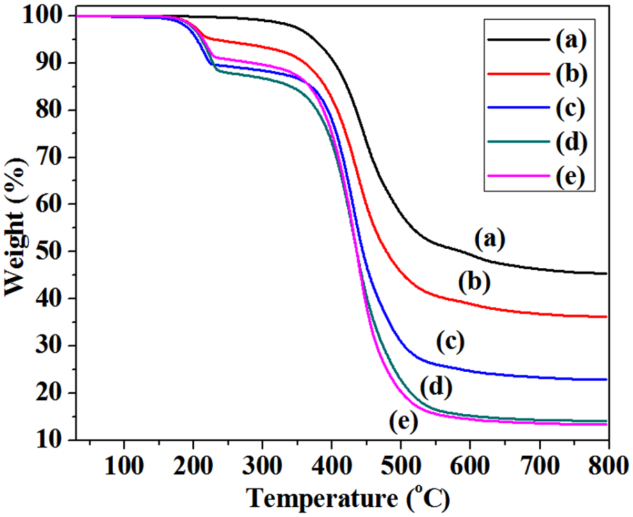

Figure 9: TG Analysis of the synthesized superhydrophobic powder obtained with various concentrations of NaOH ((**a**) PS1, (**b**) PS2, (**c**) PS3, (**d**) PS4, and (**e**) PS5).

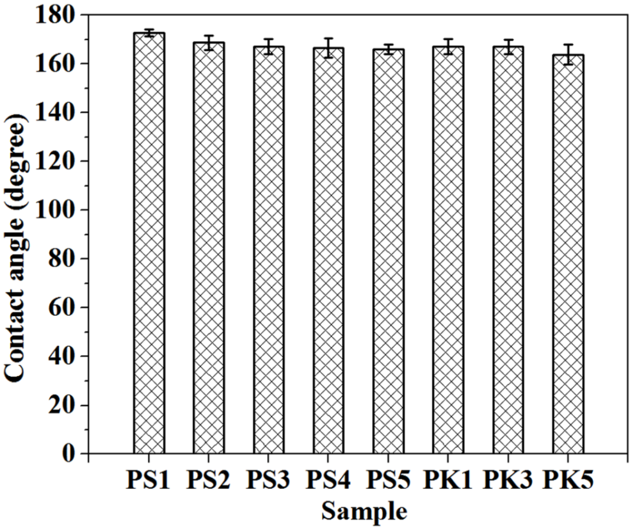

Figure 10: SCA values of the superhydrophobic powder after adding various concentration of NaOH (PS1, PS2, PS3, PS4, and PS5) or $K_2HPO_4.3H_2O$ (PK1, PK3, and PK5).

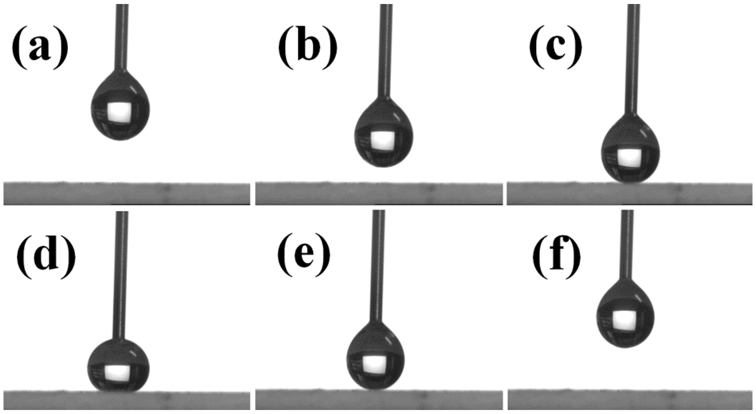

Figure 11: Optical images of a water droplet before and after adhesion and release on the superhydrophobic surface.

The superhydrophobic powder synthesized at other NaOH concentrations showed partial reduction in the thermal stability of the material (Figure **9b-e**). The maximum decomposition occurred at ~435 °C. The decrease in thermal stability by the increase in NaOH might be related to the gelation of PMHS. The enhanced gelation of PMHS under strong basic medium may hinder the formation of continuous hydrophobic siloxane chains. During this stage, the surface properties of the material were changed significantly and a partial decrease in thermal stability was observed. PMHOS powder showed superhydrophobic properties by placing a water droplet on the surface. The superhydrophobicity was checked further by coating the dispersed (in ethanol) PMHOS on a glass substrate. The coated powder exhibited a superhydrophobic contact angle (CA) of higher than 170° and non-stick properties (Figure **10**), regardless of either the NaOH concentrations or $K_2HPO_4.3H_2O$ concentrations. Figure **11** clearly shows the non-adhesion properties of the coated substrate.

4. CONCLUSIONS

Superhydrophobic PMHOS was synthesized using a one-pot approach with various concentrations of NaOH (within 2 days) or $K_2HPO_4.3H_2O$ (within 4-5 days). Gelation of PMHS did not occur after the addition of aqueous ammonia (0.1 M, 0.3 M and 0.5M) or HCl (0.1 M, 0.3 M and 0.5M) in the presence of ethanol and water. Increasing the concentration of NaOH leads to a shorter gelation time (from 8 hr to 2 hr). On the other hand, a significant decrease in the gelation time (96-120 hr) occurred after introducing $K_2HPO_4.3H_2O$. PMHOS maintained a mesoporous (Type IV hysteresis loop) structure at all NaOH concentrations. The powder showed complete non-adhesive surface properties on a coated glass substrate. The static contact angle (SCA) confirmed the formation of superhydrophobic powder by the use of NaOH or $K_2HPO_4.3H_2O$. The results showed that the hydrolysis and condensation of the Si-H groups in PMHS are strongly dependent on the concentrations of NaOH for the rapid synthesis of superhydrophobic powder. On the other hand, increasing the concentration of NaOH resulted in a significant change in the surface properties and particle size. An optimized superhydrophobic powder was synthesized successfully by using various concentrations of NaOH and $K_2HPO_4.3H_2O$ based on the present experimental procedure. The superhydrophobic powder can be also reproduced rapidly by the removal of solvent immediately after the gelation of the siloxane polymer at 150 °C.

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