Journal of Particle Science and Technology 6 (2020) 25-36

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Journal of Particle Science and Technology

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A spray pyrolysis method for fabrication of superhydrophobic copper substrate based on modified-alumina powder by fatty acid

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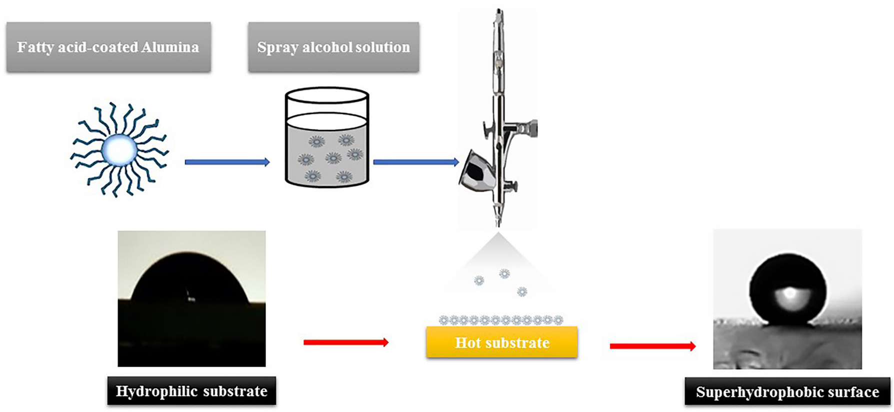
HIGHLIGHTS

- A spray pyrolysis method was developed for the fabrication of superhydrophobic copper surfaces with dispersed modified alumina by fatty acid in alcohol.
- The superhydrophobic copper surface is fabricated with water contact angles > 160° and contact angle hysteresis less than 3°.
- The stability of the spray suspension was discussed due to affecting the morphology and roughness of the deposited films.
- It is shown there is an optimum alcohol solvent (based on the hydrophobicity of alcohol) for preparing a superhydrophobic surface.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 13 April 2020
Revised 19 December 2020
Accepted 25 January 2021

Keywords:

Superhydrophobic
Copper
Alumina
Fatty acid
Spray pyrolysis

ABSTRACT

Superhydrophobicity is the tendency of a surface to repel water drops. Due to this unique property, superhydrophobic surfaces can be used in many applications, such as water-resistant surfaces, antifogging surfaces, anti-icing surfaces, and anti-corrosion surfaces. In this study, superhydrophobic surfaces were fabricated by a spray pyrolysis method with water contact angles > 160° and contact angle hysteresis less than 3°. For this purpose, the alumina nanoparticle modified by a fatty acid was dispersed in an alcohol solvent and coated on the substrate. Palmitic acid and stearic acid were selected as the modifying hydrophobic agents on the alumina surface. The chemical bonding between the surface of the alumina and the fatty acid was confirmed by Fourier-transform infrared spectroscopy (FT-IR) patterns. The influences of alcohol solvents on spray pyrolysis deposition of the modified-alumina were also studied by altering alcohol solvents (methanol, ethanol, and 2-propanol). Dynamic light scattering (DLS), scanning electron microscopy (SEM), and roughness analysis results showed that the increase in stability of spray suspension can enhance the coverage of films, which consequently increase the roughness and hydrophobicity of the layers. Wetting measurements showed that stearic acid is a better hydrophobic agent for modifying the surface of alumina, and 2-propanol is a convenient alcohol solvent for the fabrication of a superhydrophobic surface due to the highest water contact angle and lowest surface free energy of its film. The method is both easy and inexpensive, and we propose that this work has potential industrial applications for the fabrication of superhydrophobic surfaces on the various scale of copper substrates.

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DOI:10.22104/jpst.2021.4168.1168

1. Introduction

Due to its unique properties in repelling water, the fabrication of superhydrophobic surfaces has recently attracted significant interest for a variety of practical applications, including self-cleaning [1,2], anti-fogging [3], anti-icing [4], and drag reduction [5]. A superhydrophobic surface has a water contact angle (WCA) larger than 150° with a contact angle hysteresis (CAH) or a sliding angle less than 10° [6]. Therefore, the roughness and surface energy of the samples are essential parameters to achieve superhydrophobic properties [8].

Copper and copper alloys are applied in energy conversion devices (HVAC systems, vehicular coolers, radiators, heat sinks for electronic equipment cooling, etc.) [9-11]. Due to the environmental corrosion of copper and copper alloys, fabricating their superhydrophobic surfaces can be very important for practical applications [12]. Currently, two approaches are used to fabricate a superhydrophobic copper surface. One method is coating directly on a copper substrate, and the other is chemical treatment [13]. While chemical treatment is still used, the development of a new method of direct coating is necessary due to complex processes such as etching, in which wet or dry oxidation steps are followed by the deposition of low-surface energy compounds like silanes, fluoroalkyl silanes, or long-chain organic acids. In this regard, the spray pyrolysis method is a simple and inexpensive deposition method that can be applied directly on a large scale of various substrates.

Alumina is a ceramic material used in several types of coating applications because of its excellent properties, such as chemical stability, a high degree of hardness, and low cost. These properties cause alumina to be a desirable material for the fabrication of superhydrophobic films. Alumina is challenging to use in the practical applications mentioned above due to its hydrophilicity and high surface energy [14]. There are fatty acids, such as stearic acid (SA), found in the waxy layer on leaves. These fatty acids have been used to modifying the surface of metal oxides to reduce their surface energy [15-27].

Fatty acids are inexpensive and environmentally friendly materials with low surface energy. There are numerous studies of metal oxides being modified by fatty acid to fabricate superhydrophobic surfaces such as ZnO [15,16], $CaCO_3$ [17,18], and Al_2O_3 [5,19]. Although there are several reports on superhydrophobic zinc oxide modified by fatty acid [15,16,23-25,31-33], there are not many studies on superhydrophobic modified-alumina fatty acid surfaces. Richard *et al.* prepared a fabricated superhydrophobic surface with a WCA of 156° and a sliding angle less than 2° [19]. They modified-alumina with stearic acid sprayed on a glass substrate and showed that this work has the potential to be applied to cotton fabric [19]. Taghvaei *et al.* sprayed a dual-layer micro-and nanoparticle of alumina modified by SA with a WCA of 158° on aluminum sheets etched by HCl solution for drag reduction applications [5]. The first step in the spray method is the dispersion of particles in the dispersion medium. The dispersion medium is a key parameter to control the agglomeration of the particles, which can greatly affect the properties of the layer. Despite the importance of the dispersion medium on the preparation of spray suspension, comprehensive studies on this issue have not been done so far [20,21].

It should be noted that stearic acid has been used as a hydrophobic agent to modify the surface of metal oxide in many works [15-19,24,25,27,31,32], and palmitic acid (PA) has been proposed as an alternative to SA for the fabrication of better superhydrophobic surfaces [33].

In this study, a direct coating by the spray pyrolysis method is used to fabricate a superhydrophobic surface. Methanol (CH_4O), ethanol (C_2H_6O), and 2-propanol (C_3H_8O) were selected to study the effects of the dispersion medium on the wetting of the prepared samples. Also, PA and SA were selected as modifying agents on the alumina surface to compare the influence of the fatty acid carbon-chain length on the hydrophobicity of the prepared samples. Two different approaches were used to exam the effects of various alcohol solvents on the wetting of the samples. In the first approach, the modified-alumina by SA or modified-alumina by PA was dispersed in different alcohol solvents and then sprayed on the substrates. In the second approach, the fatty acid (SA or PA) was dissolved in different alcohol solvents and then sprayed on the substrates.

The results showed that the dispersion medium (for the modified-alumina by fatty acid) and solution (the fatty acid) had a significant effect on the wetting of the layer. Increasing the stability of the spray suspension enhanced coverage of the film and rougher layer, which increased the WCA. Increasing the carbon chains of the solvent or an increase in the non-polarity of the solvent causes the suspension to be more stable. On the other hand, we found that SA is the better agent for modifying the alumina surface compared to PA, which was mostly due to the lower surface energy of the SA layer. As a result, a superhydrophobic surface for a copper substrate was fabricated based on the dispersed modified-alumina nanoparticle by SA in 2-propanol with a WCA > 160° and CAH < 3°.

2. Experimental

2.1. Materials

Alumina nanoparticles (99.9%) with an average particle size of < 50 nm and surface area of the 40 m^2/g, methanol (99.9%), ethanol (99.9%), and 2-propanol (99.9%) were purchased from Merck Company. Palmitic acid and stearic acid (from CARLO EBRA, 99%) were used as received.

2.2. Sample preparation

Copper sheet was cut in 25 mm length and 15 mm width and washed ultrasonically for 10 min in acetone, ethanol, and distilled water, respectively. To prepare the modified-alumina, 0.1 g of alumina nanoparticle was dispersed in 1 wt% fatty acid (SA or PA)-ethanol solution. The suspension was stirred for 8 h. Next, it was centrifuged and washed with ethanol. Then, the spray suspension was prepared by dispersing the modified-alumina nanoparticle by fatty acid in 20 mL of an alcohol solvent. The air pressure of the spray (Airbrush, Taiwan, HD-132) was 25±5 psi. The distance of the spray nozzle from the substrate and nozzle diameter was 15 cm and 0.3 mm, respectively. The deposition temperature of the spray was 100 °C and the deposition time of spray was 90 s with a thickness of 11-12 µm. Also, the annealing temperature of the coated substrate was kept at 100 °C for 1 h.

2.3. Characterization methods

The chemical structure of the samples was obtained by Fourier-transform infrared spectroscopy (FT-IR) spectroscopy (Tensor 27, Equinox 55, Bruker). Dynamic light scattering (DLS) analysis was used to measure the particle size distributions (PSD) obtained from the HORIBA SZ-100 Dynamic Light Scattering and the Zeta potential analyzer of the modified-alumina suspension with different alcohol solvents. For measuring the thickness and roughness of the deposited films, a Nano Pajouhan Raga Surface Profilometer was used in three different positions on the samples. The film thickness was measured by forming a step between the film and the uncovered substrate. Morphology of the deposited surfaces was studied by scanning electron microscopy (SEM), HITACHI S-4160. To study the wettability of the prepared surfaces, the sessile drop technique was used with 5 µL distilled water droplets on the samples. The captive method was applied to measure the CAH at three different positions of samples (pumping into and out of a water droplet on the samples). The WCA and CAH were determined by Image J software.

3. Results and discussion

3.1. Characterization of fatty acid-coated alumina powder by FT-IR technique

Fig. 1 shows the FT-IR spectrum of alumina nanoparticles and the prepared samples with modified-alumina by fatty acid (SA or PA). According to Fig. 1, for alumina nanoparticles, the peaks at 3200-3500 cm^{-1} show the H-bonded Al-OH group, and the peaks at 746 and 1072 cm^{-1} are assigned to O-Al-O and Al-O bonds, respectively [26]. For the modified-alumina, the peaks at 1583 and 1463 cm^{-1} are attributed to the symmetric and antisymmetric stretchings of carboxylate [19,22], where the difference of 120 cm^{-1} between peaks indicates that the stearate groups adopt a chelate bidentate arrangement on the surface of the particles [27]. The peaks around 2918 cm^{-1} (CH_3) and 2850 cm^{-1} (CH_2) indicate the presence of long-chain aliphatic groups [23]. The band at 727 cm^{-1} shows angular deformation of OH and C-O-H bonds, and the peak at 908 cm^{-1} is attributed to (CH_2) rocking modes [26]. The absence of the carbonyl stretch of fatty acid (SA or PA) around 1702 cm^{-1} and the appearance of two peaks around 1583 and 1463 cm^{-1} confirm the chemical bonding took place between the alumina and the fatty acid [15].

3.2. Wetting of coated films

The wettability of rough surfaces can be explained with Wenzel and Cassie-Baxter models. The Wenzel model can be used when a liquid drop can penetrate and fill the grooves of a rough surface, as Eq. (1) [11].

$$\cos\theta_{rough} = r \cos\theta_{smooth} \tag{1}$$

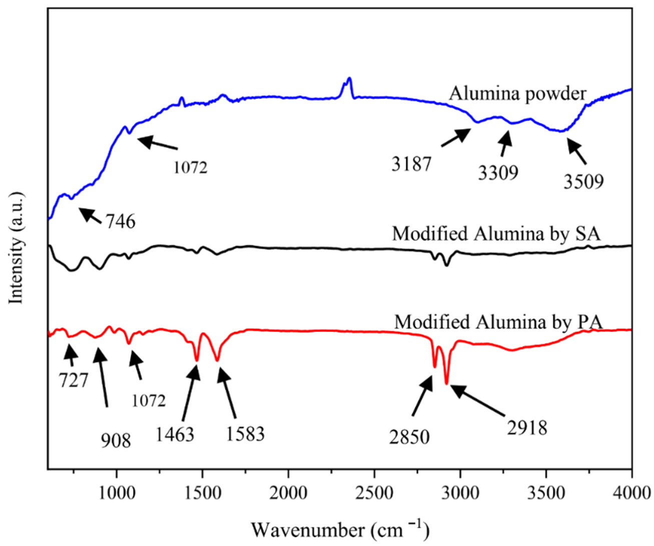

Fig. 1. The FT-IR spectra of alumina nanoparticle and as-prepared samples with modified-alumina by fatty acids PA or SA (deposition time 90s, deposition and annealing temperatures 100 °C).

where r is the ratio between the surface area and its horizontal projection, and θ_{rough} and θ_{smooth} are the WCA of rough and smooth surfaces, respectively. In superhydrophobic surfaces, air can be trapped in the grooves of a rough surface, and liquid drop can't penetrate and fill it. In this state, the hydrophobicity of the surface can be increased because trapped air reduces the interface between the surface of the solid and liquid. The Cassie-Baxter model normally can be used for a surface with a WCA > 120° by Eqs. (2) and (3) expressions [17].

$$cos\theta_{rough} = f_1\,(cos\theta_{smooth} + 1) \tag{2}$$

$$f_1 + f_2 = 1 \tag{3}$$

where f_1 and f_2 are the area fractions of surface between the liquid and air, respectively. The surface free energy (Y_w) of the surfaces was calculated by using the expression as in Eq. (4) [40].

$$Y_w = \frac{y(1+\cos\theta)^2}{4} \tag{4}$$

where y is the surface tension of water (72.8 mN.m^{-1}), and θ is the WCA of the surface. The surface free energy is an important parameter that determines the properties of a surface, such as wetting and adhesion [40]. For copper, the surface free energy is 47.8 mN.m^{-1}, which indicates the surface of the copper has more tendency to attract water. The water drop on the surface of the copper is at Wenzel state (Fig. 2(a)). After spraying the modified-alumina with a fatty acid, the samples showed a greater tendency to repel water due to decreasing the surface free energy of copper, and we can observe a transition of the water drop from a Wenzel to a Cassie-Baxter state (Figs. 2(b) and 2(c)). Compared to the modified-alumina by PA with a WCA ~ 153° and a CAH up to 9° (Y_w = 0.32 mN.m^{-1}), modification of alumina with SA reduced the surface free energy of copper better with a WCA around 161° and a CAH of less than 3° (Y_w = 0.05 mN.m^{-1}). The WCA of smooth SA coated copper was measured around 83.5 (θ_{smooth}) [19]. Using the Cassie-Baxter model, values of f_1 and f_2 of the modified-alumina by SA sample were calculated at 0.05 and 0.95, respectively. This means that 95% of the contact area between the water drop and the rough surface is occupied with air, and this state provides the self-cleaning property of the surface.

Another important parameter to determine the wettability of a surface is surface adhesion which indicates the molecular attraction of connected surfaces. Surface adhesion was calculated by using Young-Dupre's equation, as Eq. (5) [41].

$$W_{sl} = y\,(1+ cos\theta) \tag{5}$$

where W_{sl} is the work of adhesion between solid and liquid surfaces. For copper, W_{sl} is 117.6 mN.m^{-1}, and after spraying the modified-alumina it decreased to 9.75 and 3.96 mN.m^{-1} for modified-alumina by PA and modified-alumina by SA, respectively.

3.3. Investigating the stability of the fatty acid-coated alumina on wetting of films

Two approaches were studied to examine the effects of deposition solvent type on the wettability of surfaces. In the first, modified-alumina by fatty acid (PA or SA) was dispersed in an alcohol solvent and then sprayed on the copper substrates. In the second, a 1 wt% fatty acid (PA or SA)-alcohol solution was sprayed directly on the copper substrates. In both approaches, methanol, ethanol, or 2-propanol was used as a deposition alcohol solvent. The wettability of a surface is governed by the chemical composition and geometry of the solid surface [8,37]. In our samples, the chemical composition of the samples was the same, and altering deposition solvent affected the morphology and roughness of the

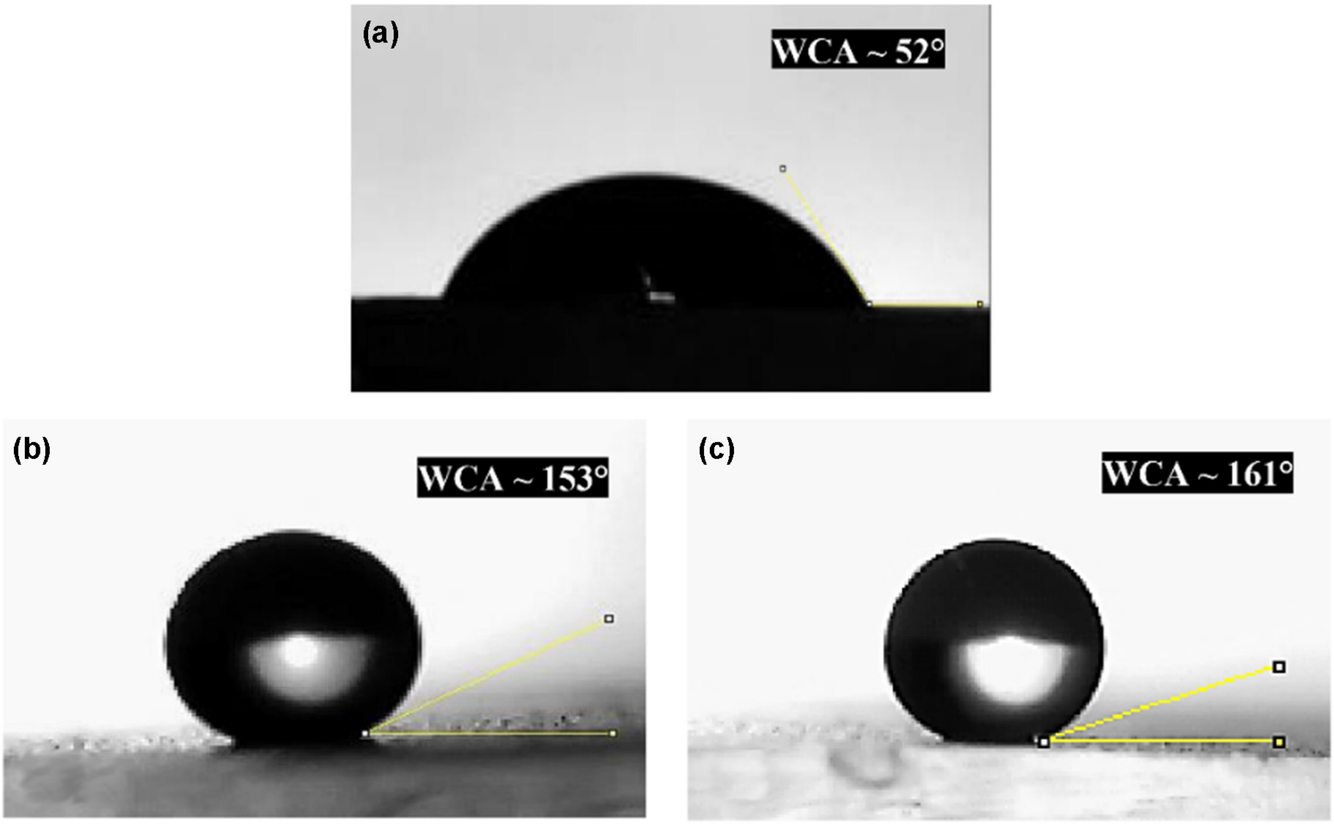

Fig. 2. The water contact angle (WCA) images of (a) copper, (b) fabricated sample with modified-alumina by PA, and (c) fabricated sample with modified-alumina by SA.

deposited film. It should be mentioned that atomic force microscopy characterization failed in these samples due to a large amount of roughness of the deposited films, and a 2D line profilometer was applied instead to measure the roughness of samples (Fig. 3). The moving average (solid lines) of the profiles was calculated with the average roughness (R_a), root-mean-square roughness (R_q), and the peak-valley difference (R_f).

The WCA, CAH, surface free energy, surface adhesion, and roughness results are listed in Table 1. There is an increase of WCA and R_q from 132° and 1895.2 nm to 161° and 4873.2 nm as a result of altering the alcohol solvent from methanol to 2-propanol for the modified-alumina by SA. Modified-alumina by SA samples have better performance in comparison with modified-alumina by PA samples, and we reached a superhydrophobic surface by spraying modified-alumina by SA in 2-propanol solvent (Y_w = 0.05 mN.m^{-1} and W_{sl} = 3.96 mN.m^{-1}).

Fig. 4 shows the DLS analysis of the modified-alumina suspension before spraying. As can be seen, the tendency of particles to aggregate increased when using a less hydrophobic alcohol solvent (methanol). For example, in 2-propanol, the PSD of the modified-

Table 1. Water contact angle (WCA), contact angle hysteresis (CAH), surface free energy (Y_w), surface adhesion (W_{sl}), and roughness parameters of modified-alumina samples (deposition time 90 s, deposition and annealing temperatures 100 °C).

Spray suspension	WCA (degree)	CAH (degree)	Y_w (mN.m^{-1})	W_{sl} (mN.m^{-1})	R_a (nm)	R_q (nm)	R_f (nm)
PA-Alumina in methanol	128.5	26.1	2.59	27.48	929.8	1313.9	4102.6
PA-Alumina in ethanol	144.4	22.6	0.63	13.6	2159.2	2162.6	4182.2
PA-Alumina in 2-propanol	153.8	9.5	0.19	7.53	3417.3	3873.3	6161.9
SA-Alumina in methanol	132.7	18.4	1.88	23.42	1626.7	1895.2	7629.7
SA-Alumina in ethanol	147.6	12.2	0.47	11.74	2542.6	3105.7	7361.2
SA-Alumina in 2-propanol	161.7	2.7	0.05	3.96	4187.4	4873.2	9094.8

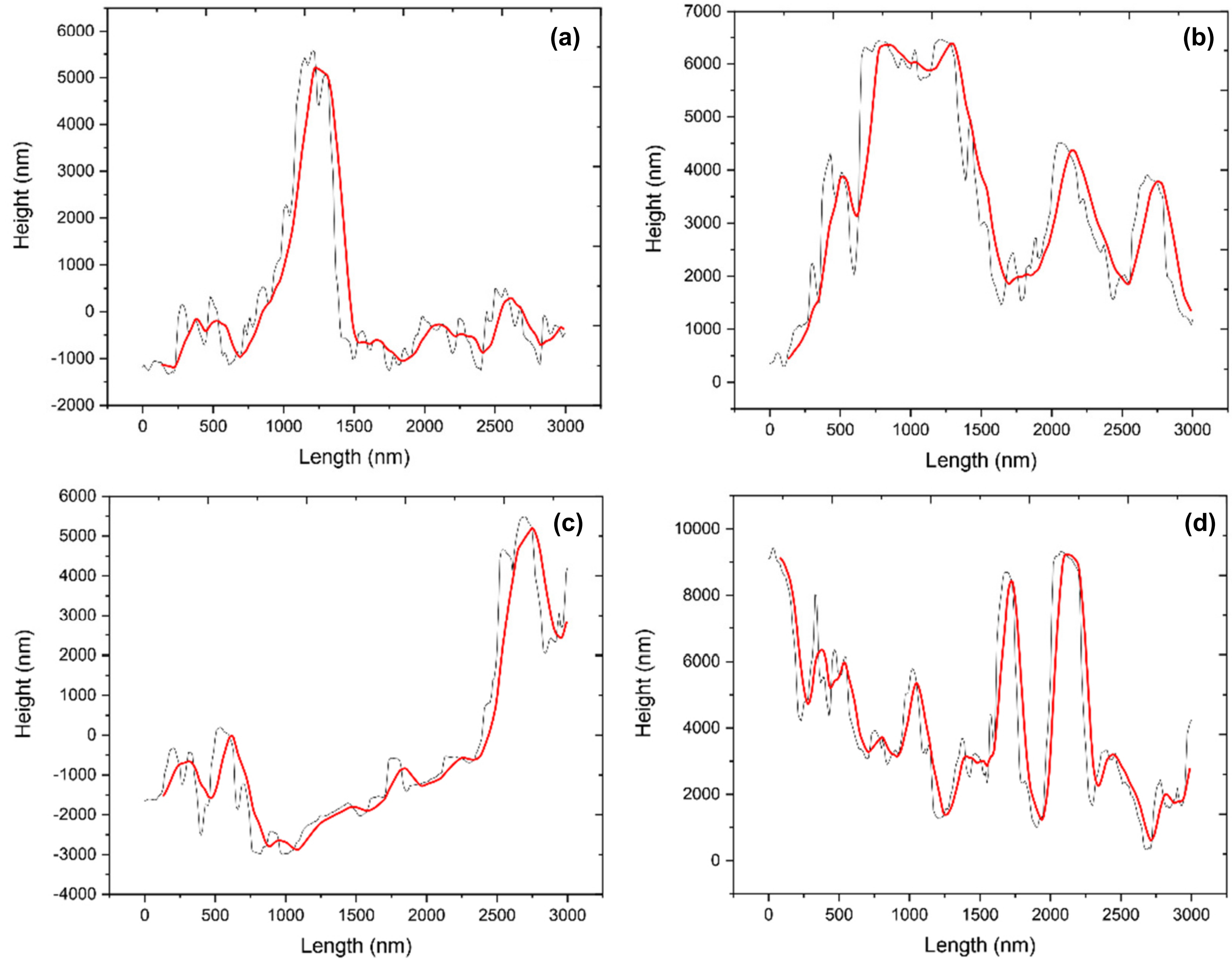

Fig. 3. 2D line surface roughness graph of the fabricated sample by (a) modified-alumina by PA in methanol solvent, (b) modified-alumina by PA in 2-propanol solvent, (c) modified-alumina by SA in methanol suspension, and (d) modified-alumina by SA in 2-propanol solvent (deposition time 90 s, deposition and annealing temperatures 100 °C).

alumina by SA suspension is approximately 96 nm, but in methanol, it increased to 184 nm. Moreover, modified-alumina by SA has less tendency to aggregation in comparison with modified-alumina by PA in various alcohol solvents.

According to the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, the stability of the modified-powder by fatty acid is based on van der Waals attractive energy (V_A) and the osmotic repulsive energy (V_R). The V_A is the attraction energy from the van der Waals force between two particles. Also, the V_R is an important parameter for the repulsive energy of modified particles with fatty acid [26]. As it was mentioned, the stability of the modified-alumina by the fatty acid suspension is based on the osmotic repulsive mechanism, which can be increased by increasing the alkyl chain length in fatty acids [26,27]. In our case, the more alkyl chain of SA enhanced the V_R between particles.

SA has a longer carbon chain length than PA. This causes the modified-alumina by SA suspension to become more stable than the modified-alumina by PA, and according to roughness calculations, it dramatically affects the roughness of the deposited layers. As a result, the more stable modified-alumina by SA suspension in 2-propanol caused the sample to have high surface coverage, and consequently, high roughness in comparison with other samples.

Fig. 5 shows SEM images of the prepared samples (modified-alumina by fatty acid films) in two magnifications. Figs. 5(a) and 5(b) show the flaky structure of the modified-alumina by PA samples. Spraying modified-alumina by PA in the methanol solvent covered the surface of the copper non-uniform (Fig. 5(a)) due to more aggregated particles. Figs. 5(c) and 5(d) show the flake-like and the hierarchical rod-like microstructure, respectively. Similar to

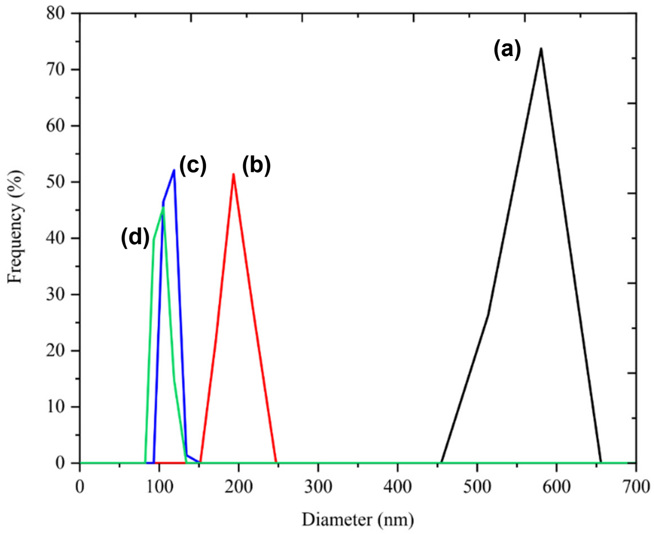

Fig. 4. Particle size distribution (PSD) of prepared suspensions before spraying. (a) modified-aumina by PA in methanol (530 nm), (b) modified-alumina by SA in methanol (184 nm), (c) modified-alumina by PA in 2-propanol (106 nm), and (d) modified-alumina by SA in 2-propanol (96 nm).

the modified-alumina by PA samples, there is a big difference between spraying modified-alumina by SA in the methanol and the 2-propanol to cover the surface of copper due to various aggregation states of particles. These results show a highly unstable suspension can affect the coverage of film due to the high aggregation state of the particles, and this process decreases the roughness of the deposited film.

In Table 2, WCA, CAH, surface free energy, and surface adhesion of the prepared samples by the fatty acid solution are listed. According to Table 2, by altering alcohol solvent, we see that an adequate alcohol solution (2-propanol) is observed to fabricate hydrophobic surfaces with the fatty acid solution. Altering the alcohol solvent from methanol to 2-propanol increased the WCA from 125° to 128° for the PA's samples and from 114° to 135° for the SA's samples. By comparing the WCA and CAH of the samples, altering the alcohol solvent is more effective on the WCA and CAH of the SA's samples than the PA's samples.

Fig. 6 shows the SEM images of the samples in two magnifications. By altering the deposition solvent, the morphology of the deposited surface was affected remarkably. For instance, according to the small-scale images of Figs. 6(a) and 6(b), the PA-methanol sample has a special microscale flower-like structure, and the PA-2-propanol sample has a flower-like microstructure composed of macro sheets. Fig. 6(d) shows the flower-like morphology of the SA-2-propanol sample composed of micro-sheets, where the morphology of deposit film is similar to blooming flowers.

The solubility of fatty acid in alcohol solvents is based on the polarity of solvents and the carbon chain length of the fatty acid [28-30]. Increasing the polarity of solvents decreases the solubility of fatty acids [28]. In other words, increasing the chain length of the fatty acid decreases the solubility of the fatty acid in the alcohol solvents due to the increasing non-polarity of the fatty acid [29,30]. Altering the deposition solvent has an impact on the solubility of the fatty acid solution, and this process can affect the aggregation state of a fatty acid solution [35,36]. The SA-methanol solution must have a high aggregation state, and as can be seen in Fig. 6(c), the deposited film has a smooth and uniform morphology.

It can be concluded that altering the deposition solvent controls the aggregation state of fatty acid, and this process affects the porous interconnection of the deposited film. We observe an interconnected porosity for the SA-methanol sample (Fig. 6(c)), which has decreased WCA in comparison with other samples. The water drop is in the Wenzel state, which means this structure can't hold air pockets and water droplets can penetrate the grooves of a rough surface and spread out over the copper substrate. The 2-propanol

Table 2. Water contact angle (WCA), contact angle hysteresis (CAH), surface free energy (Y_w), and surface adhesion (W_{sl}) of fatty acid solution samples (1 wt% fatty acid solution, deposition time 90, and deposition temperature 50 °C).

Spray solution	WCA (degree)	CAH (degree)	Y_w (mN.m^{-1})	W_{sl} (mN.m^{-1})
PA-Methanol	125.7	30.9	3.15	30.31
PA-Ethanol	126.5	30	2.98	29.49
PA-2-Propanol	128.8	27.7	2.53	27.18
SA-Methanol	114.4	35.7	6.26	42.72
SA-Ethanol	131.9	20.9	2.01	24.18
SA-2-Propanol	135.1	15.3	1.54	21.23

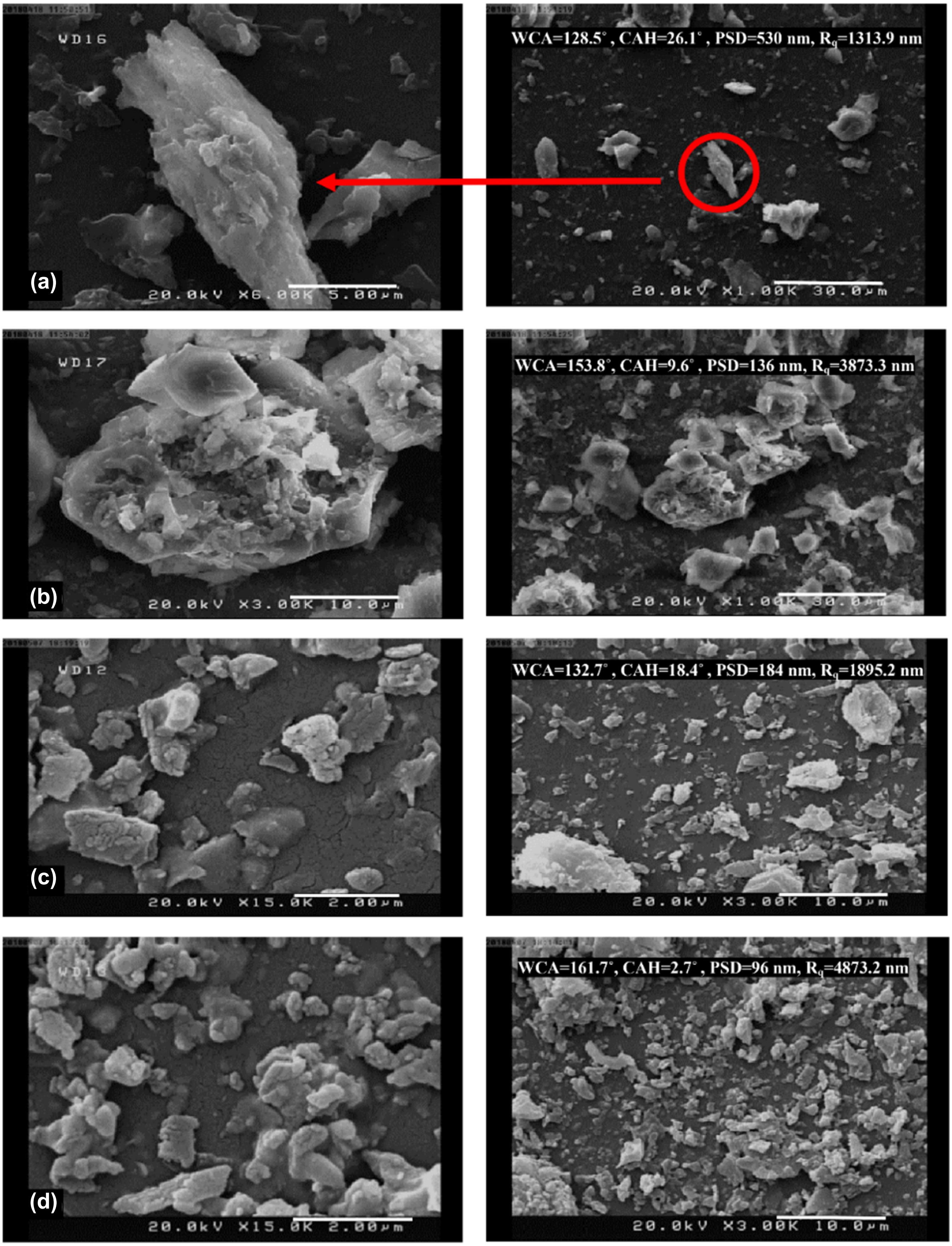

Fig. 5. The SEM images of (a) fabricated sample by spraying modified-alumina by PA in methanol solvent, (b) fabricated sample by spraying modified-alumina by PA in 2-propanol, (c) fabricated sample by spraying modified-aumina by SA in methanol, and (d) fabricated sample by spraying modified-alumina by SA in 2-propanol (deposition time 90 s, deposition and annealing temperatures 100 °C).

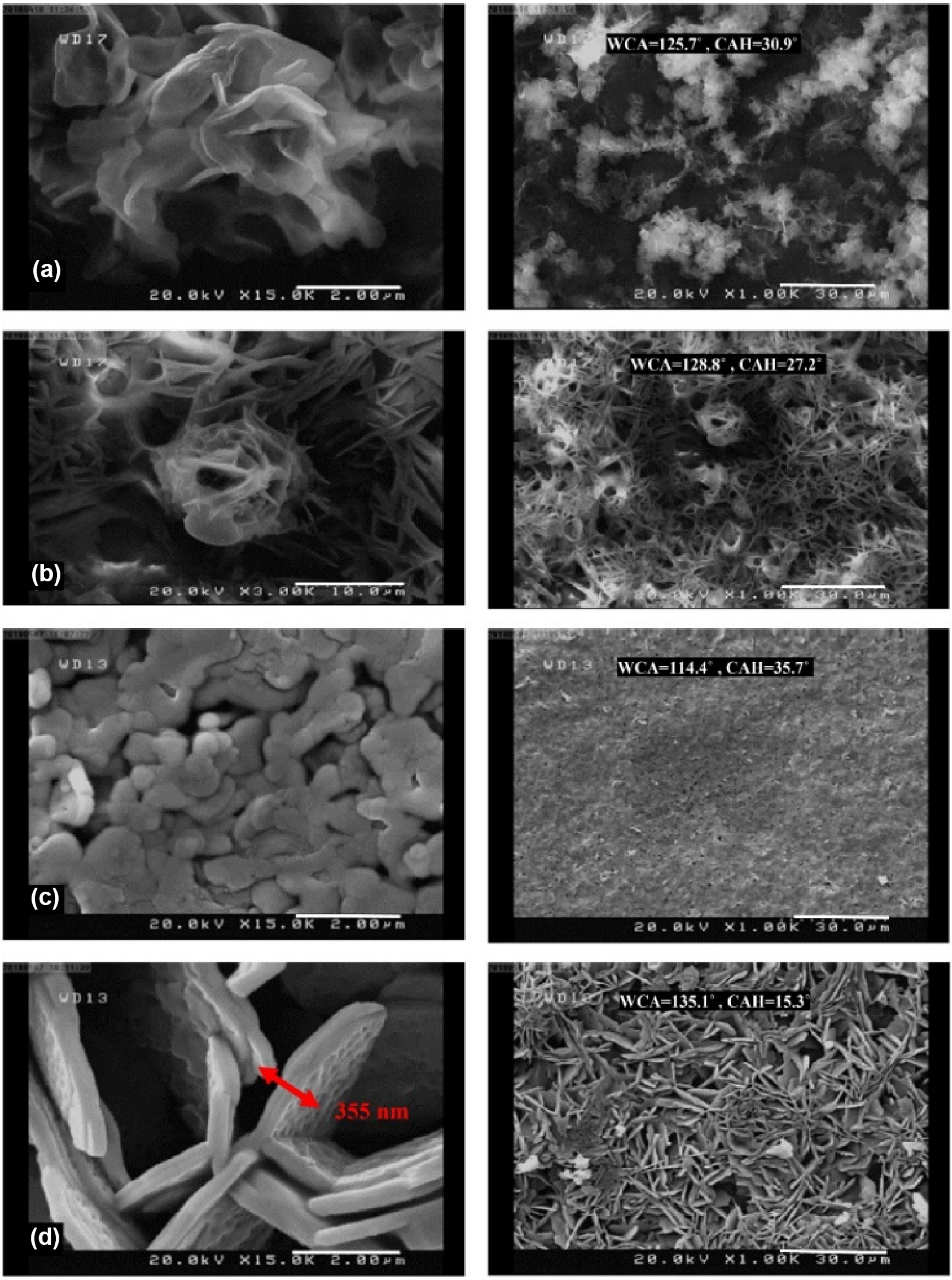

Fig. 6. The SEM images of the samples fabricated by (a) spraying PA-methanol solution, (b) spraying PA-2-propanol solution, (c) spraying SA-methanol solution, and (d) spraying SA-2-propanol solution (1 wt% fatty acid solution, deposition time 90 s, and deposition temperature 50 °C).

solvent is seen to be an adequate deposition solvent in both approaches. Based on the carbon chain length of the fatty acids or hydrophobic polymers, it can be concluded that there is an optimum alcohol solvent (based on the hydrophobicity of alcohol) for preparing a spray suspension of the coating.

3.4. Superhydrophobic copper surface

In Fig. 7, this spray method was utilized on a copper substrate. As can be seen, water drops (dyed blue on the surface of the substrate) on the substrate are in the Cassie-Baxter state, which indicates that this method can be applied to fabricate the superhydrophobic surface of the copper substrate on a large scale.

4. Conclusion

In this research, superhydrophobic modified-alumina by stearic acid surfaces was fabricated by a spray pyrolysis method (water contact angle > 160°). Systemic examination of the deposited alcohol solvent showed that there is an adequate alcohol solvent (2-propanol) for preparing the spray suspension. It was observed that stearic acid is a better hydrophobic agent than palmitic acid to modify the surface of alumina for the fabrication of a superhydrophobic surface. In addition to other parameters of deposition, our study demonstrated that the deposition solvent should be considered an important parameter of spray pyrolysis deposition on the fabrication of superhydrophobic surfaces due to its effect on the morphology and roughness of the deposited film, and it can be concluded that, based on the carbon chain length of the fatty acids or hydrophobic polymers, there is an optimum deposition alcohol solvent for preparing spray suspension and the fabrication of a superhydrophobic surface.

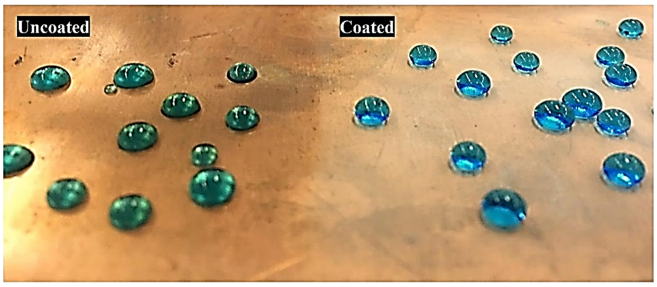

Fig. 7. The superhydrophobic surface of the copper substrate (deposition time 90 s, deposition and annealing temperatures 100 °C).

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