Superhydrophobic surface for dropwise condensation is prepared using hotplate solution immersion method on copper substrate. The preprocessed bare copper plate is immersed in a solution consist of 0.004 – 0.008M ethanol (CH$_3$−CH$_2$−OH) and tetradecanoic acid (CH$_3$(CH$_2$)$_{12}$COOH) then heating the plates in the solution at 30 – 50°C for 1 – 6 hours. The contact angle of water droplet on the prepared surface is measured using Low Bond Axisymmetric Drop Shape Analysis (LBADSA), which gives the maximum contact angle of 168° and average value of 166° ± 2°. The maximum contact angle is obtained by adjusting the composition of the solution, temperature of the solution and immersion time to 0.006M, 45° and 4 hours respectively. The various superhydrophobic surfaces are prepared by changing constituents of solution, hotplate temperature and processing time respectively. Further dynamic behavior of water droplet on the prepared surfaces like jumping effect and rolling effect is presented in this work. In addition, experimental work is carried out on the prepared surface for dropwise condensation and the obtained results are compared with condensation on bare copper plate produces higher heat transfer coefficient.

Key words: Superhydrophobic copper surface, contact angle, water droplet jump, rolling angle, dropwise condensation.

1. Introduction

Dropwise condensation produces high heat transfer coefficient than the film wise condensation and enriches fast removal of thermal energy from the working fluid on condenser surface. Thus, dropwise condensation is an important mechanism for phase change heat transfer can be used in many applications like heat exchangers, electronic device cooling, power generation, refrigeration and air conditioning. Schmidt et al. [1] first reported the dropwise condensation in 1930. Rose [2] analysed the mechanism of dropwise condensation and reported the heat transfer coefficients of dropwise condensation is 5–10 times higher than that of filmwise condensation.

Dropwise condensation can be promoted by adding a non-wetting chemical into the vapor [3], by special physical treatment of the condensation substrate [4], or by chemical coating of the solid substrate with a low surface-energy substance [5-6]. These techniques have been known for many years; the last technique holds considerable promise and has been an active area of research. Vemuri et al. [6] experimentally investigated the effects of various chemical coatings and their long term
durability on the dropwise mode of heat transfer. Ucar and Erbil [7] investigated the effect of surface roughness, wettability, contact angle hysteresis and wetting hysteresis of different polymeric surfaces. In recent years, Starostin et al. [8] prepared the superhydrophobic surface on aluminium substrate and reported the kinetic growth of droplets on superhydrophobic surface. Kim et al. [9] studied air-cooled condensation experiment inside a bare and tetrafluoroethylene coated Pyrex glass tube. They reported the local heat flux values on coated tube were higher than the bare tube in the upstream region. Yanagisawa et al. [10] prepared a superhydrophobic surface with random nanoscale roughness using boehmite nanoparticles and analysed spontaneous jumping of the condensed water droplets from top and side directions. Roudgar and Coninck [11], investigated experimentally for dropwise condensation on copper substrate and reported that, in the early stage of condensation, condensation contact angle and contact angle hysteresis have an important effect on the nucleation and the condensation rate.

Vilaro et al. [12] fabricated solventless two-steps process superhydrophobic copper surfaces using chemical vapor deposition method and was able produce the contact angle of 163° for around one day. Xu et al. [13] fabricated a simple and safe one-step immersion method to obtain the stable superhydrophobic surfaces on copper substrate using an organic alkali, N-dimethylcyclohexylamine. The time duration for surface preparation is more than two days with the maximum contact angle about 160°. Bahramia et al. [14] prepared superhydrophobic copper surfaces by an oxidation process with NaClO2, NaOH and Na3PO4•12H2O then modified with 1-Octadecanethiol. They examined the effects of oxidation time, modifier concentration, and modification time for the contact angle 161° with the preparation time of around 30 hours. N. Xu et al. [15] coated superhydrophobic films on an aluminum alloy surface via a one-step electrochemical modification process in an ethanolic stearic acid solution containing copper nitrite (Cu(NO3)2) under a DC voltage. Various morphologies were obtained when different molar ratios of the solution and obtained maximum contact angle of 162°. X. Xu et al. [16] fabricated superhydrophobic copper surface by a simple wet-chemical etching and self-assemble method. They discussed the effect of surface structure on fabricating superhydrophobic surface with the maximum contact angle of 151°. Feng et al. [17] prepared the superhydrophobic copper surface for corrosion resistance by oxidizing, heat-treating, and alkyl chains’ grafting method with contact angle of 157°. Wang et al. [18] fabricated a novel stable bionic superhydrophobic surface just by immersing a copper plate into a solution of fatty acids at ambient temperature with a high water contact angle of about 162°.

In the present work the superhydrophobic surface is prepared on copper plates which produce the maximum water contact angle of about 168° by simple thermo solution immersion method within the time period of 4 hours. Different samples of ethanol (CH3−CH2−OH) and tetradecanoic acid (CH3(CH2)12COOH) solutions 0.004M, 0.006M and 0.008M respectively, are used to prepare superhydrophobic surface for different time and temperatures. The water contact angle is measured by Low-Bond Axisymmetric Drop Shape Analysis (LBADSA) method developed by Stalder et al. [19]. Further, the dynamic behavior of jumping of water droplet and sliding of water droplet on prepared surfaces and a bare copper substrate are examined. Sample of 0.006M solution produces average contact angle of about 166° ±2° and the sliding angle of around 4°. An experimental setup is developed for analyzing and observing the phenomenon of dropwise condensation underneath the condensed substrate. Then the experiment is conducted to obtain dropwise condensation and compared the heat transfer coefficient of superhydrophobic surface with bare copper substrate.
2. Surface preparation

The different processes for the preparation of superhydrophobic surfaces, contact angle $\theta \geq 150^\circ$ as shown in Fig.1(a), have been used, such as electrochemical deposition, plasma method, crystallization control, laser and sputtering techniques, physical metal removal techniques, chemical vapor deposition, wet chemical reaction, sol-gel processing, lithography and solution immersion processes. In the present work, simple one step solution immersion method on hotplate is used for the preparation of superhydrophobic surface on copper substrates.

Wang et al. [10] conducted an experiment to produce superhydrophobicity on copper plate using solution immersion process in which a copper plate was immersed in an ethanol solution of n-tetradecanoic acid (0.01 M) at room temperature for 3 to 5 days. Their experiments suggest that a concentration of around 0.01 M is ideal for the formation of stable flowerlike clusters. When the concentration is about 0.001 M, a self-assembled monolayer of tetradecanoic acid is formed on the copper substrate and the contact angle is only about 124$^\circ$. At above 0.02 M, the microclusters or nanosheets prefer to form in solution rather than on the copper plates. Thus, the concentration of tetradecanoic acid is crucial for the formation of flowerlike clusters. They concluded with concentration of 0.01 M which gives a high Contact angle of about 160$^\circ$. The drawback of their work is it requires high concentration of 0.01 M and five days to form superhydrophobic surface on copper plate compared with our work it required only 0.004M – 0.008M low concentration and less time of around one to six hours. After immersing the superhydrophobic surface in water, acetone, ethanol and toluene for 5 days, we obtained unchanged contact angle about 166$^\circ$.

In the present work the superhydrophobic surface, with maximum contact angle of about 168$^\circ$ at 0.006 M solution within 4 hours, is obtained on a copper substrate by using hotplate solution immersion process. Initially the plate is cleaned to remove the impurities on the copper plate. Then the solution is prepared for required composition and concentration. The cleaned copper plate is then immersed into the solution and the plate is heated by hot plate for certain constant temperature with atmospheric pressure. After heating the plate for certain time, the plate is taken out of the hot solution and cleaned with first acetone, second ethonal, third deionized water and then dried with air. The self-assembled monolayer is formed on the copper plate which produces superhydrophobic nature followed by Cassie-Baxter model as shown in Fig. 1(b).

2.1. Procedure for preparing superhydrophobic surface on copper substrate

The processes involved in preparing superhydrophobic surface on copper substrate is shown in Fig. 2. The copper plate of required size (25 x 25 x 3 mm) is first rubbed with rough emery sheet and
later with fine emery sheet. Then the plat is kept in ultrasonic bath with acetone for 10 – 15 minutes. After rinsed with deionized water the plate is dipped in hydrochloric acid for 2 – 3 minutes. After rinsing the plate with deionized water, the plate is then dried with air. Then the plate is immersed in a solution of 0.004 – 0.008M of ethanol and tetradecanoic acid. The solution immersed plate is heated in a hot plate at 30 – 50°C for one to five hours and rinsed with deionized water and ethanol superhydrophobic layer is formed on the surface which produce the average contact angle of about 166° ± 2°.

![Figure 2. Surface preparation processes](image)

The processes shown in Fig. 2 is repeated for different molarity, temperature and time of immersion as given in the Table 1. The samples consist of the molarity of 0.004 M, 0.006 M and 0.008 M solution of ethanol and tetradecanoic acid respectively. Each sample is heated at the different temperatures and immersion time varying from 30 – 50°C and 1 – 6 hours respectively. The corresponding higher contact angle against the applying temperatures is listed in Tab. 1. The larger contact angle obtained from the molarity 0.006 M at 45°C for 4 hours of heating.

<table>
<thead>
<tr>
<th>Molarity (M)</th>
<th>Temperature (°C)</th>
<th>Higher contact angle (±2°)</th>
<th>Immersion time (hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.004</td>
<td>30</td>
<td>146</td>
<td>6</td>
</tr>
<tr>
<td>35</td>
<td></td>
<td>148</td>
<td>6</td>
</tr>
<tr>
<td>40</td>
<td></td>
<td>150</td>
<td>6</td>
</tr>
<tr>
<td>45</td>
<td></td>
<td>148</td>
<td>6</td>
</tr>
<tr>
<td>50</td>
<td></td>
<td>145</td>
<td>6</td>
</tr>
<tr>
<td>0.006</td>
<td>30</td>
<td>152</td>
<td>5</td>
</tr>
<tr>
<td>35</td>
<td></td>
<td>156</td>
<td>4</td>
</tr>
<tr>
<td>40</td>
<td></td>
<td>161</td>
<td>5</td>
</tr>
<tr>
<td>45</td>
<td></td>
<td>166</td>
<td>4</td>
</tr>
<tr>
<td>50</td>
<td></td>
<td>155</td>
<td>5</td>
</tr>
<tr>
<td>0.008</td>
<td>30</td>
<td>160</td>
<td>1</td>
</tr>
<tr>
<td>35</td>
<td></td>
<td>159</td>
<td>1</td>
</tr>
<tr>
<td>40</td>
<td></td>
<td>158</td>
<td>1</td>
</tr>
<tr>
<td>45</td>
<td></td>
<td>156</td>
<td>1</td>
</tr>
</tbody>
</table>
It is noted that the highest contact angle is obtained from the sample-2, 0.006 M, heated at 45°C for 4 hours. After post processing, the sample-2 is analysed in Scanning Electron Microscopy (SEM) and the obtained images are shown in Fig. 3. The ethanol and tetradecanoic acid solution is reacted with copper substrate and self-assembled monolayers are formed on the copper substrate like pieces of nano sticks as shown in Fig. 3(a-c) with different magnifications from 20µm to 1µm. The lower growth of monolayers with the molarity of 0.004 M solution is not able to produce Cassie-Baxter model and 0.008 M solution produces larger growth of monolayers, which leads to decrease in contact angle. The temperature is also affect the growth rate and assembled layer structures to form heterogenous surface which leads to the Cassie-Baxter model [20]. The lower molarity, sample-1, with lower temperature produces lag in the growth rate of monolayers and able to produce only hydrophobic surfaces for the given time periods 1 – 6 hours. In case of higher molarity, sample-3, and lower temperature, the superhydrophobic surfaces contact angles (θ>150°) are produced. Sample-2 is able to produce the maximum contact angle about 168° at 45°C for 4 hours heating the solution.

2.2. Contact angle measurement

Contact angle is measured by a powerful tool for characterizing three-phase junctions. The technique of the sessile drop is today the most widely used method to measure this parameter. The commercial software available today are still very limited. They are often dependant of one measurement setup, and may fail under non-standard conditions. Stalder et al. [19,21] proposed two methods to measure contacce angles with high-accuracy, one is DropSnake, it is based on B-spline
snakes (active contours) to shape the drop and the another one is LBADSA shown in Fig. 4(a-b), it is based on the fitting of the Young-Laplace equation to the image data.

![Figure 5](image1.png)

**Figure 5.** Water droplet on (a) the bare surface and (b) the prepared surface.

In the present work the contact angles are measured using LBADSA method. Prepared surface and the bare copper surface are examined for the water contact angle and the images are shown in Fig. 5 (a-b). The bare copper surface produces the contact angle less than 90° as shown in Fig. 5 (a). The prepared surface produces the maximum contact angle of about 168° at 45°C for 4 hours of heating is shown in Fig. 5 (b).

3. Experimental setup

![Figure 6](image2.png)

**Figure 6.** Experimental setup

The experimental setup shown in Fig. 6, consist of a vacuum chamber connected to vacuum pump and water chamber for cooling the substrate at the top of the setup. The electric heater is placed at the bottom of the vacuum chamber with power regulator to develop steam in the chamber.
A CCD camera Basler with image capture Streamix software, data acquisition system with Labview software made up of National instruments are used to capture the condensation and droplet behaviors. Thermocouples of K-type with accuracy level of 0.01°C are used to measure the temperature inside the chamber and substrate temperature. The cut sectional view of the setup is shown in Fig. 7. The experiment is conducted on both bare and superhydrophobic surfaces for varying the properties like vapour temperature (Ts), surface temperature (Tw), power input (I) and cooling water flow rate (m³/hr). The maximum input power can be set by the setup is 100W by regulating with least of 1W. There are three thermocouples, shown in Fig. 7, placed in the water chamber nearer to the cooling water inlet, centre of the chamber and nearer to the outlet. The average of three temperature is taken as water temperature (Tw). The cooling water flow can be adjusted up to 500 m³/hr. In the present work, three conditions, water flow rate of 0.1 m³/hr, 0.2 m³/hr and 0.3 m³/hr are used for experimenting the dropwise condensation on superhydrophobic copper substrate. The temperatures of the vapour and surface are acquired from data acquisition system connected with the setup to the computer through labview software. The images are stored and videos are captured by the camera connected to another computer through strempix software.

4. Results and discussion

4.1. Superhydrophobic Surface

The water contact angles obtained for the different temperature and time are shown in the Fig. 8. The average contact angle on the prepared surface is obtained by taking five different spots and each
spots three different observations were made. The maximum average contact angle of 166° is obtained on the prepared surface with 0.006 M solution against the temperature around 45°C for 4 hours of heating in the solution. Further increasing the immersion time and increasing the temperature leads to decrease in contact angle due to large growth of monolayers on copper substrate. Larger the monolayers growth and temperature vanish the Cassie-Baxter model and decreases the superhydrophobic nature.

4.2. Sliding of water droplet on prepared surface

The sliding of water droplet on the prepared surface and bare copper substrate is examined by tilting the substrate from zero degree as shown in Fig. 9. A color charge coupled device CCD video camera Basler with 1024 x 1024 pixels at 117 fps was used to capture the images of the water droplet sliding on the superhydrophobic copper substrate. The LED light source placed behind the water droplets and the images are captured using Streampix software.

![Figure 9. Droplet sliding on superhydrophobic surface at an angle of 2.5° (a) at t ≈ 0 s, (b) after t ≈ 17μs, (c) after t ≈ 43μs, (d) after t ≈ 60μs](image)

In the dropwise condensation phenomenon, the sliding of droplets are important for heat transfer enhancement. The sliding of droplets induces a new condensation surface on which new small droplets are generated [22]. This means that the condition required for droplets to slide on a solid surface is related to the heat transfer efficiency. The physical conditions for which sliding of water droplet will lead to dewetting of a surface limited to superhydrophobic surface with low contact angle hysteresis. Usually, superhydrophobic surfaces will have high roughness and droplets will remain in the so-called Cassie-Baxter state where only peaks of roughness morphology will be in contact with water. This state significantly facilitates the dewetting process leads to sliding effect of water droplets with small inclination [23].

The sliding effect is examined on the prepared substrate due to its highest superhydrophobic nature on the copper substrate. The prepared copper substrate is tilted from initial horizontal position and about 2.5° the water droplet on the substrate is try to start its rolling along the surface as shown in Fig. 9 (a). The time of the water droplet at just dropped on the superhydrophobic surface is assumed as time t=0s and in the next frame droplet starts rolling along the surface due to low surface energy and non wettable nature of the superhydrophobic surface. The successive rolling of the droplet are captured and shown in the Fig. 9 (b-d) with the corresponding time t=17μs to t=60μs.
4.3. Jumping of water droplet on prepared surface

Figure 10. Droplet jumping on (a) bare surface and (b) superhydrophobic surface

The jumping effect is analysed by dropping a water droplet of diameter \( d \approx 3\) mm from the height of about \( h = 75\) mm. The impact causes the droplet to spread laterally, undergo kinetic-to-surface energy conversion due to additional surface area creation, and reach a maximum diameter at the spreading time. The droplet then undergoes the reverse process and retracts due to surface-to-kinetic energy conversion then finally lifts off the surface at the theoretical contact time \([22]\).

Fig. 10 (a) shows the water droplet dropped on bare copper substrate corresponding to the time \( t \approx 0-26\) μs. It is noted that there is zero jump due to high surface energy, wettable nature of the surface and low contact angle of water droplet which is less than 90° on bare copper substrate. Fig. 10 (b) shows that the water droplet is dropped on prepared superhydrophobic surface, which has maximum contact angle about 168°, it is clearly noted that water droplet jumps about the height of \( h = 9\) mm after the first impact at time \( t = 9\) μs. After first jump the water droplets reaches particular height and made its second impact on the substrate and continuous its three consecutive jumps and moved to the rest position. Even though it has higher contact angle there is zero jump due to the removal of water from Cassie-Baxter surfaces with differing microstructure types, which is clearly reported by Crick and Parkin \([23]\).

4.4. Dropwise condensation underneath prepared surface

First the experiment is conducted on bare copper plate. The power is given to the heater inside the vacuum chamber and regulated with different inputs from 30 – 100 W with a difference of 5 W. The cooling water flow is controlled for three conditions \( 0.1 \) m\(^3\)/hr, \( 0.2 \) m\(^3\)/hr and \( 0.3 \) m\(^3\)/hr. The values of surface temperature \( T_w \) and vapour temperature \( T_s \) are obtained and the experiment is repeated for superhydrophobic copper substrate with same conditions. The heat transfer coefficient is calculated by newton law of cooling and also compared the difference in temperature (\( \Delta T = T_s - T_w \)), water droplet falling time and heat transfer coefficient of bare plate with superhydrophobic surface.
The Fig. 11 (a) shows the condensation of bare copper plate with irregular water particles underneath the copper plate and the films are formed between the irregular water droplets which reduce the contact surface area and increases the resistance to heat flow between the vapour and the copper surface. Also the fall off diameter of the droplet is high in bare copper surface condensation due to its high surface energy of water particles with low contact angle. This cause the low heat transfer coefficient and low condensation rate. In case of Fig. 11 (b) shows the dropwise condensation on superhydrophobic surface with regular complete sphere like droplets which increase the contact surface area between the vapour and the plate surface. There is no room for the formation of films on the superhydrophobic surface instead the water particles are formed as droplets which results decrease in resistance to flow of heat and the fall off diameter of the droplet from the superhydrophobic surface. This causes the increase in heat transfer coefficient and rate of condensation.

**Figure 11. Condensation underneath (a) bare surface and (b) sample-2 surface**

**Figure 12. Difference in temperature ΔT (a) bare surface and (b) superhydrophobic surface**
Fig. 12 (a) and (b) shows the difference in temperature ΔT on superhydrophobic and bare surface for different water flow rate 0.1 m³/hr, 0.2 m³/hr and 0.3 m³/hr respectively. The value of ΔT is decreased with increase in cooling water flow rate at 0.3 m³/hr due to high thermal resistance offered by the coating layer on the copper substrate. Although the thermal conductivity of the coating layer is lower, due to difference in wetting behaviour, the heat transfer coefficient is higher for dropwise condensation on copper with thin layer than the bare copper [11]. At this flow rate the heat transfer coefficient is increased and got the maximum value of around 218 [W/m²K] shown in Fig. 14 (a). In both the cases 0.1 m³/hr conditions gives the highest difference in temperature due to low mass flow rate. In Fig. 13 (a) and (b) shows the condensed droplet falling time on superhydrophobic and bare surface for different water flow rate respectively. It shows that, about 80 seconds is required for the first condensed fall off droplet in superhydrophobic substrate, whereas, it takes about 125 seconds in case of bare surface. The condensed water droplet fall off time is about 1 second on superhydrophobic surface and 2 seconds for bare surface against the mass flow rate of 0.3 m³/hr. It is noted that the condensing rate of water particles is higher in superhydrophobic surface than the bare surface.
Fig. 14 (a) and (b) shows the comparison of heat transfer coefficient $h$ with corresponding heat input $I$ in which high amount heat transfer coefficient around 218 [Wm-2K-1] obtained in superhydrophobic surface. For the same temperature, bare surface provides around 168 [Wm-2K-1]. It is noted that, around 30% of heat transfer coefficient is increased for the same working conditions by using superhydrophobic surface. The value is still low due to the resistance offered by the coating against the heat transfer across the substrate.

5. Conclusion

Superhydrophobic copper surface with maximum contact angle of $168^\circ$ is prepared by thermo solution immersion technique with the quick time of 4 hours. The average contact angle of $166^\circ$ is obtained with the concentration of the ethanol and tetradecanoic acid of 0.006M when the solution is heated at 45°C for the time duration of 4 hours. The prepared copper substrate produces the sliding angle of $2.5^\circ$ for the water droplet rolling on the substrate. The water droplet on the superhydrophobic surface jumps about the height of $h\approx9$mm for the first jump and it continues three consecutive jumps to attain its rest condition.

The obtained surface is experimented for dropwise condensation by varying the power input and water flow rate. The complete sphere like water droplets are obtained on the condensing surface with increase in contact area, which results increase in heat transfer coefficient and condensation rate. The maximum value of temperature difference between the vapour and the surface is 77°C and 65°C for bare and superhydrophobic surface respectively. The temperature difference is inversely proportional to the heat transfer coefficient and the maximum heat transfer coefficient obtained is 218 [Wm-2K-1] for superhydrophobic surface.

References


Paper submitted: 26 January 2019  
Paper revised 18 February 2020  
Paper accepted: 24 February 2020