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DEVELOPMENT OF SUPERHYDROPHOBIC SURFACE THROUGH FACILE DIP COATING METHOD

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The focus of the present work is to fabricate and investigate the surface characteristics of a superhydrophobic surface on aluminum (Al) and copper (Cu) substrates using a facile dip coating technique. Three different samples of 'Al' and 'Cu' were prepared with chemical etching, mechanical rubbing and the combination of above two methods. The changes in surface morphologies were analyzed using surface profilometer, scanning electron microscope and energy-dispersive X-ray spectroscopy. The modified samples were dipped in an aqueous solution of silver nitrate followed by immersing in a mixture of ethanol and 1H, 1H, 2H, 2H-Perfluorodecyltriethoxysilanefor 10 min. The presence of dendrites and leaf-like structure were noticed on the surface, which are useful to trap the air between them and the entrapment allows water to roll off from the surface. The results showed that the modified substrates have a water contact angle of 165° and 158° respectively in the case of 'Al' and 'Cu' using combination of chemical etching and mechanical rubbing followed by dip coating. The proposed methodology has the advantage of size compatibility and easy scale up for the development of superhydrophobic surface on aluminum and copper in a cost and time effective manner. The fabricated superhydrophobic surfaces are more suitable for various applications like self-cleaning, condensation, etc.

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1. Introduction

The properties of metals, such as roughness and wettability, are modified by forming a hydrophobic/superhydrophobic film over the surface. The superhydrophobic surface generally refers to a combination of the static contact angle greater than 150° with a contact angle hysteresis lower than 5º [1-3]. It is classified into two types according to water rolling angle; an extremely adhesive superhydrophobic surface that allows water droplets to adhere the surface, even when the surface is turned upside down and less adhesive superhydrophobic surface with a rolling angle less than 10º [4]. The characteristics of superhydrophobic surface have been investigated, since the last decade due to its advantageous features such as energy savings, self-cleaning, anti-icing, oil-water separation, corrosion resistance, condensation heat transfer and drag-reduction [5]. Different grades of aluminum (Al) and copper (Cu) are widely used as a base material in various industrial applications for the fabrication of system components and making these surfaces into superhydrophobic would largely be beneficial, in terms of enhancing the system performance along with longer durability. Research works on superhydrophobic surface have shown a considerable progress and numerous methods have been successfully developed for the fabrication of superhydrophobic surface on a variety of metal substrates [6]. However, many of the proposed methods possess certain limitations like complex process controls, severe operating environments, requirement of special equipment and time consuming. Also, a lot of technical itches are present in the exiting techniques to develop a superhydrophobic surface on a substrate having larger surface area and complex geometry [7]. The literature pertaining to the development of superhydrophobic surface are reviewed and presented as follows; Qian and Shen reported maximum water contact of 156º in 'Al' substrate by chemical etching method [8]. The formation of flower like structures on

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the ‘Cu’ substrate by one step deposition process transformed ‘Cu’ into superhydrophobic surface with a contact angle of 153±2º [9]. Yin et al. proposed the combination of anodic oxidation, partial etching and dipping in oxosilane for the development of superhydrophobic surface in an ‘Al’ substrate and reported an enhanced corrosion inhabitation due to the presence of cracks and the stable superhydrophobic coating [10]. Latthe and Rao reported a water contact angle of 162±2° and roll-off angle 6±1° in the glass substrate with coating done using sol-gel derived SiO_2 micro-particles [11]. The transition from hydrophilicity to superhydrophilicity and superhydrophobicity was achieved in ‘Al’ alloy by acid etching followed by the coating with polypropylene [12]. A novel method to provide superhydrophobicity on ‘Cu’ sheet was developed by the combination of chemical etching and polydymethylsilaxane template that resulted water contact and sliding angle of 153º and 7º respectively, even after it exposed to sever humid conditions [13]. Various technique have been adapted to develop superhydrophobicity surface on different substrates such as zinc [14], aluminum, aluminum alloys [15-18], copper [19], glass [20-21] and steel [22]. From the above literature it is clear that the proposed methods involve complex process with more time consuming and only few methods have been reported for the development of superhydrophobic surface at micro/nano scale. Considering the fascinating features of superhydrophobic surface and the pressing need to develop a cost effective coating technique, an attempt is made in the present work to develop a superhydrophobic surface on ‘Al’ and ‘Cu’ substrates through a novel method by combining chemical etching and mechanical rubbing followed by dip coating. The surface characterization studies such as morphological feature, chemical composition, roughness and water contact angle were analyzed and reported.

2. Materials and methods

The substrates used in this study, were industrial grade aluminum and copper, each having the purity of 99%. The reagents used were silver nitrate, 1H, 1H, 2H, 2H-Perfluorodecyltriethoxysilane (PFDTES), ethanol, acetone, hydrogen peroxide and hydrochloric acid and all of them are analytical grade purchased from Sigma Aldrich, India. Initially, the substrates were polished using a surface polishing machine and the substrates were then ultrasonically cleaned at a frequency of 15 Hz in a soap solution for 5 min. Three different methods such as chemical etching, mechanical roubbing and combination of the above were adopted separately to increase the roughness of the polished surface. Chemical etching of aluminum surface (AS 1) was carried out in the aqueous solution of 1 M hydrocloric acid for 30 s and in case of copper surface (CS 1) the chemical etching was carried out in aqueous solution of hydrogen peroxide kept in the ultrasonic bath for 15 min. In mechanical roughening, the samples (AS 2 and CS 2) gently rubbed with an abrasion sheet with different particle sizes of 63µm, 35.8µm and 15.3µm. Another set of both (AS 3 and CS 3) substrates was prepared by using a combination of mechanical rubbing followed by chemical etching. In each case, the prepared samples were cleaned ultrasonically using ethanol, acetone and distilled water and the samples were kept in an oven for 10 min. Afterwards, the samples were immersed in 0.5 M aqueous solution of silver nitrate for 5s followed by dipping, in a mixture of ethanol and PFDTESfor 10 min. The samples were then placed in an oven at a temperature of 200ºC for one hour to make them dry. The samples were then characterized using different techniques as described in the following sections.

3. Results and Discussion

The surface morphology of all samples was examined by scanning electron microscope (Tescon vega-3) and their roughness was measured by a surface profilometer (Talysurf Cci Lite) as illustrated in Fig. 1. The presence of scratches and pits were noticed in both polished ‘AS’ and ‘CS’ with the roughness value of 0.039µm and 0.017µm respectively as shown in Fig. 1(a). It is seen that the inherent closely packed grain structures in ‘CS’ resulted lower roughness than ‘AS’. As depicted in Fig. 1(b), the step like structures were found on the surface of ‘AS’ and in the case of ‘CS’ the pits were irregularly placed with larger size, than the polished surface due to chemical etching that leads to an increase in the roughness ratio of 0.77µm from 0.039µm for ‘AS’ and

0.457μm from 0.017μm for 'CS'. During chemical etching, the 'Al' and 'Cu' got etched with an aqueous solution of hydrochloric acid and hydrogen peroxide respectively. From the results of EDX, traces of carbon and oxygen are present on the surface as shown in Fig.2 (d), that have been developed by the interaction between etched surfaces with the atmosphere. When the etched surface was exposed to the dip coating, dendrites on the 'AS' and leaf like structure on 'CS' were formed as shown in Fig.1(c) that leads to an increase in roughness value. The formation of the structure was mainly due to the presence of silver and functionalization with a low-surface-energy PFDTESas shown in Fig.2 (e).

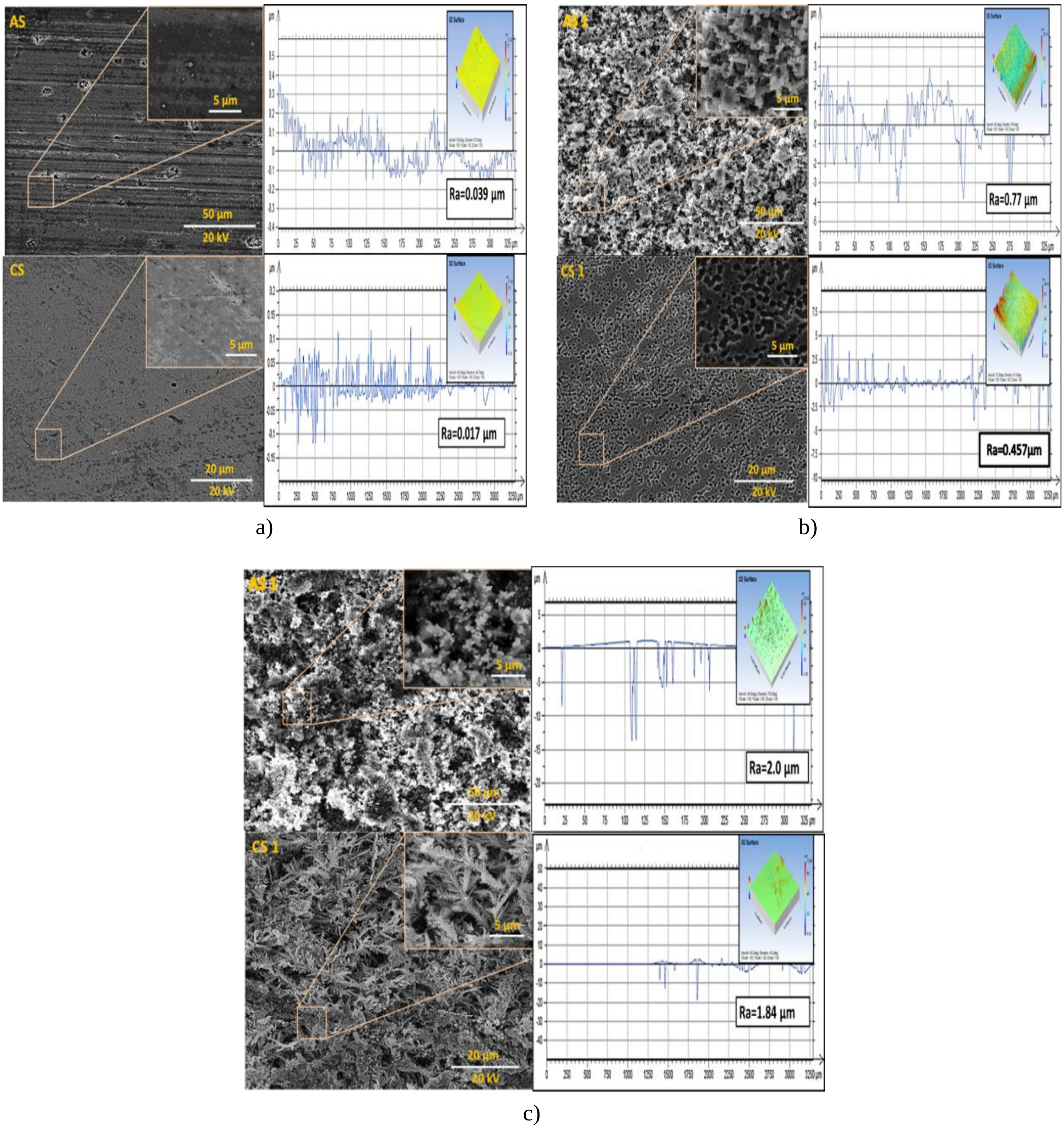
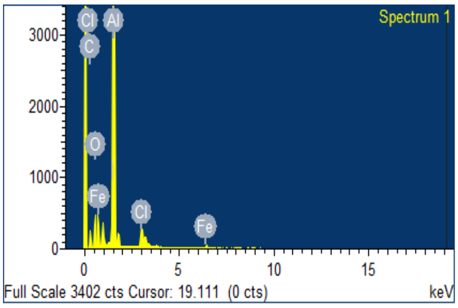
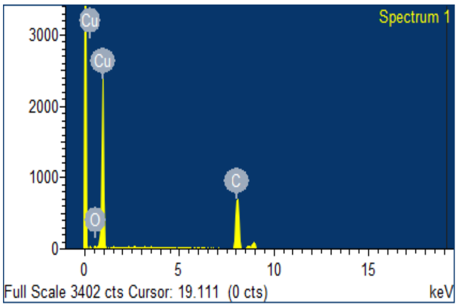


Fig. 1 SEM and surface roughness of the studied samples
(a) Polished; (b) Chemical etching; (c) Coated surface after chemical etching

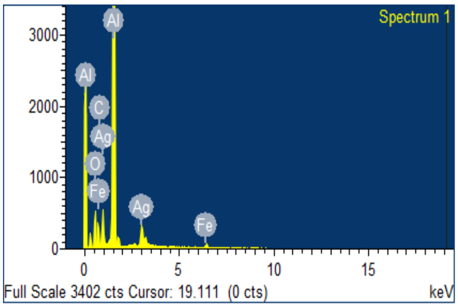


Element	Atomic%
C	6.84
O	10.10
Al	69.58
Cl	13.19
Fe	0.29
Total	**100.00**

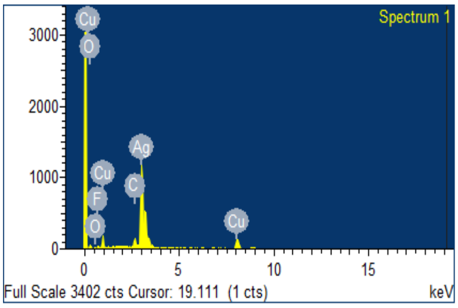


Element	Atomic%
C	15.59
O	8.45
Cu	75.96
Total	**100.00**

a)



Element	Atomic%
C	5.45
O	7.96
Al	59.79
Fe	0.32
Ag	26.48
Total	**100.00**



Element	Atomic%
C	6.35
O	9.76
F	5.33
Cu	47.78
Ag	30.78
Total	**100.00**

b)

Fig. 2 EDAX representations of the samples (a) Elements after chemical etching; (b) Elements in coated surface after chemical etching

Figure 3(a) shows the surface modification of ‘AS’ and ‘CS’ obtained with mechanical rubbing and the roughness increases considerably in both samples. The existence of micro grooves, scratches and pits were noticed and the larger grooves were present in ‘AS’ owing to the loosely packed grain structure than the ‘CS’ surface. By combining mechanical rubbing and etching, it is observed that the value of roughness increased to 1.14μm and 0.602μm for ‘AS’ and ‘CS’ as shown in Fig.3 (b). A similar increase in roughness along with dendrites and leaf like structure on ‘AS’ and ‘CS’, respectively was achieved by mechanical rubbing followed by coating as presented in Fig.3(c). It is interesting to note that the adoption of etching, mechanical rubbing and dip coating resulted with the maximum increase of surface roughness as illustrated in Fig.3 (d) that would be beneficial to develop the superhydrophobic surface.

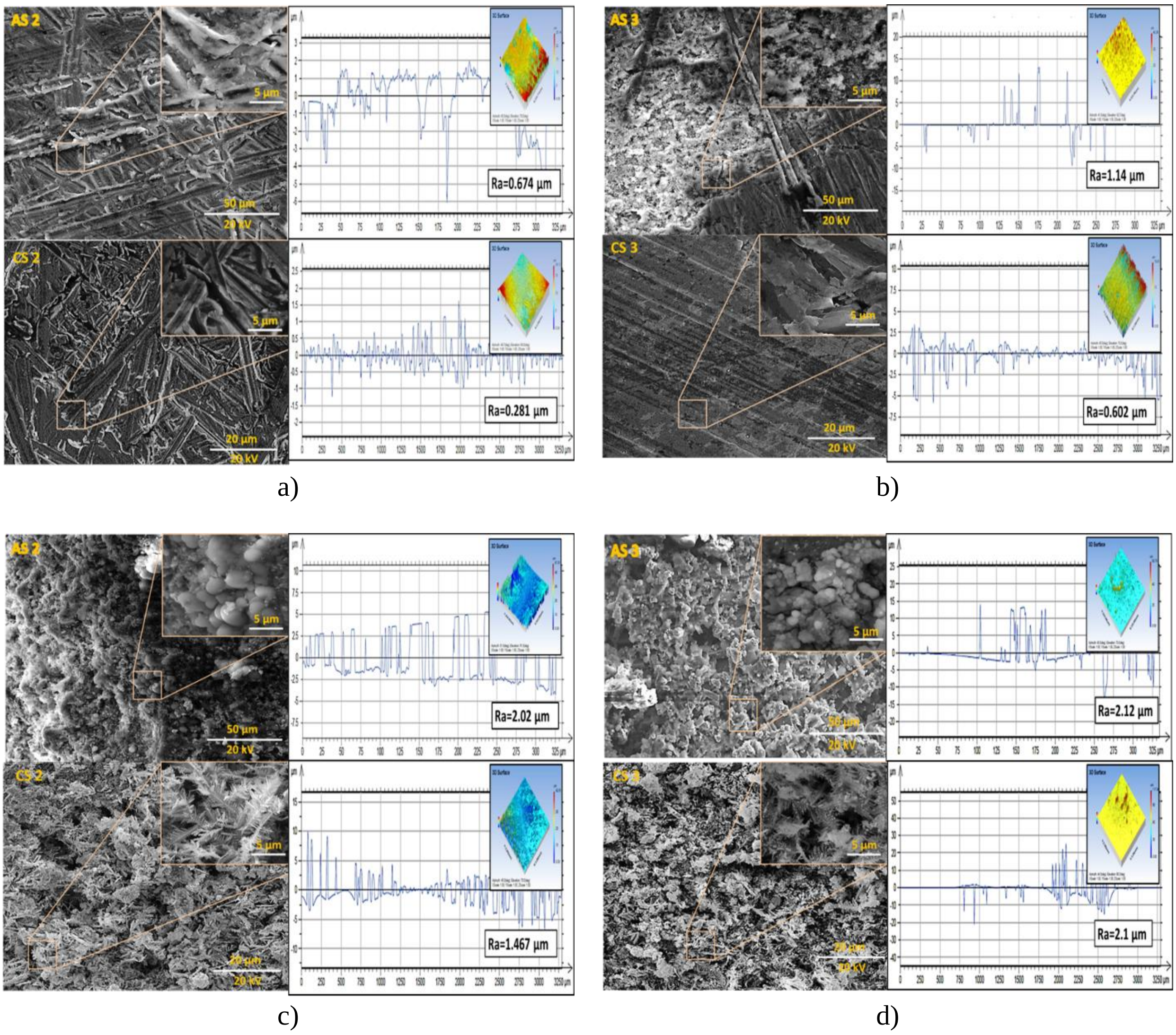
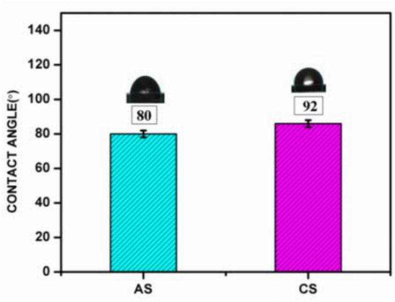
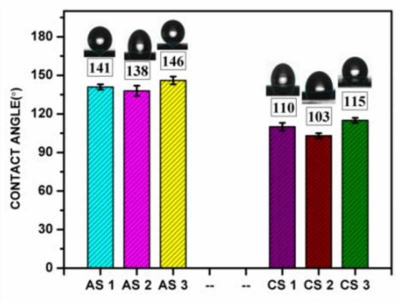


Fig.3 SEM and surface roughness of the samples (a) Mechanical rubbing (b) Combination of chemical etching and mechanical rubbing (c) Coated surface after mechanical rubbing (d) Coated surface after chemical etching followed by mechanical rubbing.

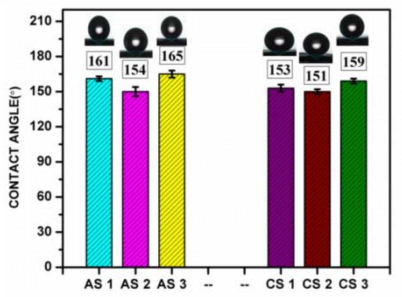
The wettability of the substrate was measured, in terms of contact angle, using a Goniometer (Data physics–OCA 20) based on sessile drop measuring method. A droplet size of 5µl was taken and the contact angle was measured at six different positions in a sample maintained at a temperature of 30ºC. It is observed from Fig. 3(a) that the contact angle of polished surface was found to be 80º and 92º in the case of ‘AS’ and ‘CS’ respectively. The superhydrophobicity was not attained in both substrates by chemical etching, mechanical rubbing and combination of above, since the contact angle of 150º was not achieved as observed in Fig. 3(b). This is due to non-creation of micro/nano structure on the surface that does not allow the water droplets to roll off easily. However, the contact angle increased gradually due to the coating that forms the dendrites and leaf structures to trap air between them that enables the water droplet to roll off the surface more easily. The corresponding contact angles are presented in Fig. 3(c) and it lies in the range between 150º to 165º. From the above results, the surface with PFDTES coating enhance the superhydrophobicity through the creation of micro/nano metric structures and these structures are stable on the substrates due to the presence of siloxane bonds in PFDTES.



(a)



(b)



(c)

Fig. 3 Contact angle measurements for (a) Polished surface (b) Before coating (c) After coating.

The durability of hydrophobicity nature for both (Al and Cu) substrates were studied and analyzed under ambient (25-30ºC), low (5-10ºC) and high temperature (105-110ºC) conditions for 45 days respectively. It can be inferred from Figure 4 and Figure 5 that for all the temperature conditions the hydrophobicity nature for both the substrates remains unchanged. Based on the above discussion, it is construed that the proposed coating method is the most beneficial in developing the superhydrophobic surface even on the substrates with large surface area and complex geometry in a cost effective manner.

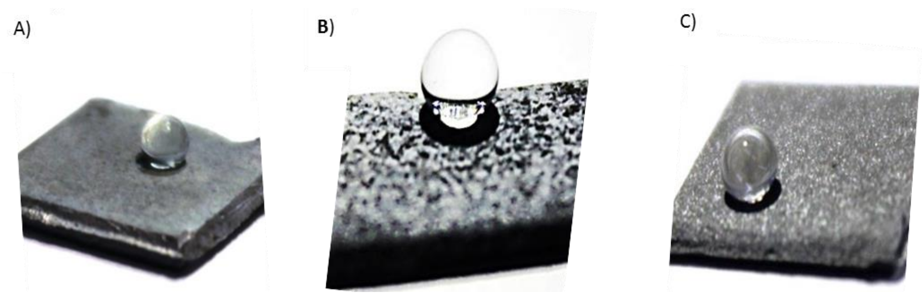


Fig. 4 Hydrophobic nature of Al substrates at (A) ambient temperature, (B) low temperature and (C) high temperature respectively after 45 days.

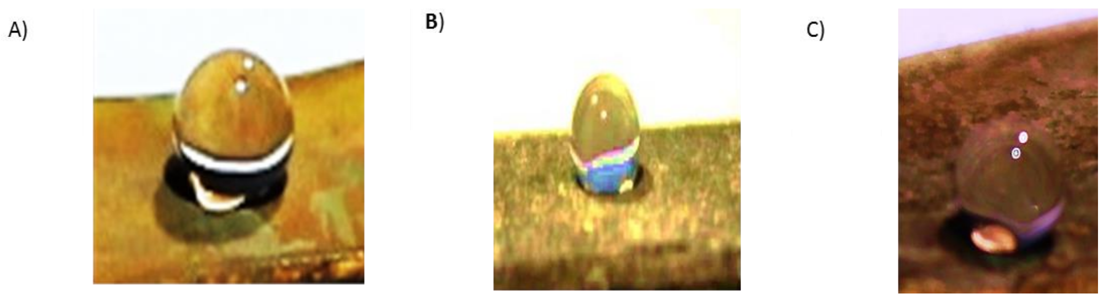


Fig.5 Hydrophobic nature of Cu substrates at (A) ambient temperature, (B) low temperature and (C) high temperature respectively after 45 days.

4. Conclusions

In summary, superhydrophobic surfaces were successfully developed by a simple dip coating technique. The substrates subjected to combination of chemical etching and mechanical rubbing found to be more suitable than the substrates modified by chemical etching and mechanical rubbing separately. The surface modification results reveal that the substrates were covered with dendrite and leaf like structure along with the presence of cracks at micro/nano scales through surface modification followed by dip coating. The increase in water contact angle was due to entrapment of air between the dendrite/leaf like structure or cracks which make water to roll of easy away from the surface. The method proposed in the present work has an advantage of compatibility and easy scale up for the development of superhydrophobic surface on aluminum and copper in a cost effective manner, which finds a lot of applications in various energy intensive sectors.

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