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**COMMUNICATION**

# Self-cleaning and superhydrophobic CuO coating by jet-nebulizer spray pyrolysis technique

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**We demonstrate for the first time the fabrication of superhydrophobic CuO coating with excellent self-cleaning ability by custom-made jet nebulizer spray pyrolysis technique. A stable Cassie-Baxter superhydrophobic wetting state (water contact angle ~154°) was maintained even after high speed water jet impact on monoclinic CuO crystallite coating, which realize the robust feature of coating. The mist-type aerosol distribution from nebulizer controls the resultant morphology of CuO film and thereby tuning the superhydrophobic property. The low-cost (~1$) portable pocket-size nebulizer affords the reliable CuO superhydrophobic coatings onto wide range of desired host surface.**

Superhydrophobic self-cleaning surfaces are attracting enormous attention due to their potential in industrial applications. Water drops eventually roll off the superhydrophobic surface due to their extremely high contact angles ($\theta$ > 150-160°).[1] The contaminants accumulated on such surfaces can be easily detached and washed off by the instantaneously rolling spherical water droplets. This surface self-cleaning behaviour is famously acknowledged as '*Lotus effect*'.[2] In nature, lotus leaf perform outstanding self-cleaning behaviour due to its excellent superhydrophobic property and therefore the lotus leaf remains clean and shiny for forever.[3] This excellent non-wetting property of lotus leaf is mainly due to the well-covered low surface energy wax material on the micro/nanoscale hierarchical surface structure. Such natural self-cleaning superhydrophobic surfaces can be artificially developed by simply lowering the surface energy of rough solid surfaces.[4] Three wetting states can be generally observed on the rough solid surfaces, namely Wenzel's state (sticky hydrophobic, no water drop rolling)[5], Cassie-Baxter's state (non-sticky superhydrophobic, water drop rolling at low sliding angles) [6] and metastable Cassie-Baxter's state (sticky superhydrophobic, water drop rolling at high sliding angles).[7]

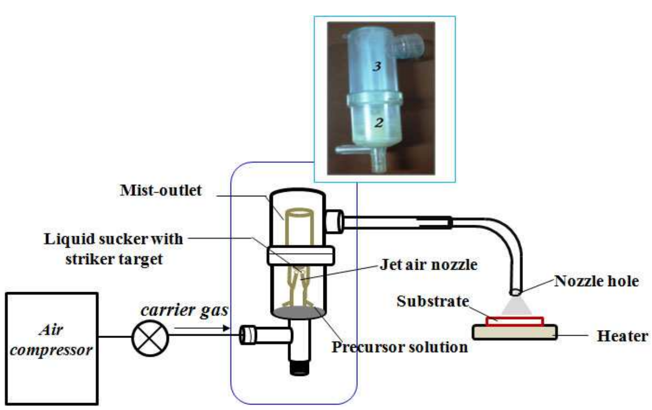
Copper oxide is p-type semiconductor material composed of two different oxide phases, such as cuprous oxide (CuO) and cupric oxide ($Cu_2O$). Owing to their excellent optical and electrical properties it has been widely progressed in gas sensors, energy storage devices, solar cells, photocatalyst, field emission device and superhydrophobic coatings.[8] In addition, biocompatibility nature and earth abundant copper resource foster CuO coatings as self-cleaning coating in biomedical devices and oil/water separation membranes.[9] Switching the CuO wetting behaviour from superhydrophilic to superhydrophobic or vice versa is the state of art in surface coatings. Li *et al*[9c] tuned the wettability of superhydrophobic CuO surface from non-sticky to sticky superhydrophobicity by controlling CuO microflower/nanorod array structures *via* simply immersing the copper plates in a mixture of aqueous potassium hydroxide and ammonium persulfate solution and subsequent modification by fluoroalkylsilane for 24 h. Under appropriate post chemical treatment on CuO, it showed excellent transition wetting behaviour from superhydrophobic to hydrophilic.[10] For instance, Chaudhary *et al*[9d] demonstrated the mixture of sodium hydroxide and ammonium persulfate aqueous solution for surface oxidation on copper sheet. The resultant CuO surface prepared by 30 min of immersion in alkali solution showed water contact angle of 159°, whereas the superhydrophilicity (< 10°) was achieved by 3 min of oxygen plasma treatment. The instantaneous storage in dark for 72 h regained the superhydrophobicity. The analogues wetting transition between superhydrophobicity and superhydrophilicity was explored on non-flaking CuO nanowires surface by Zhang *et al.*[9e] They utilized air-plasma and surface fluorination treatment for achieving superhydrophilicity and superhydrophobicity, respectively. Recently, Zhang and co-workers[9f] have developed durable superhydrophobic CuO surfaces by simply etching the copper substrates in nitric acid, immersing in platinum tetrachloride aqueous solution and subsequent annealing at 180 °C. The resultant CuO surface showed water contact angle of 170° and almost 0° of sliding angle, without subsequent low surface energy chemical modification. Furthermore, the metal salt/polymer composite was also employed as surface modifying agent for achieving superhydrophobic CuO surface.[11] Apart from chemical treatment, electrochemical technique was also practiced for obtaining superhydrophobic CuO surface using Cu metal plates.[9a]

Despite the conversion of Cu metal to CuO showed effective superhydrophobic surface it could require appropriate post chemical treatment as well as inadequate in transforming these coating on any other desired host material. Therefore, it necessitates the development of feasible coating technique, which affords robust superhydrophobic surfaces without any additional post-treatment. In this context, the spray pyrolysis technique is simple and effective for large area coating on any desired host surface.[12] In particular, jet-nebulizer spray (*j-NS*) technique is feasible in producing pin-hole free, uniform coating through controlling aerosol droplet distribution.[13] Moreover, less material consumption with better spray control than pneumatic spray pyrolysis technique renders the *j-NS* technique highly competitive in large scale superhydrophobic commercial coatings. In this work we demonstrate the facile fabrication of robust and superhydrophobic CuO coatings on glass substrates instead using copper substrate or plates. The wetting behaviour of CuO surface is finely tuned by spray coating duration. Water drops placed on *j-NS* spray coated CuO surface displayed Cassie-Baxter's wetting state and their stability is analyzed with water jet impact. To the best of our knowledge, this is the first report on *j-NS* derived superhydrophobic CuO coatings and a stable Cassie-Baxter superhydrophobic wetting state was maintained even after high speed water jet impact.

The CuO oxide films were prepared by *j-NS* technique as is shown in Scheme 1. Unlike conventional spray gun, the nebulizer set up affords precise control in droplet size distribution of the aerosol. Applying high carrier gas pressure (1 $Kg/cm^3$) through nebulizer the spray solution is transported to nozzle cone followed by the continuous coating. The liquid sucking cone with small hole (marked as 2 in the inset of Scheme 1) and outlet with 1cm in diameter of cone nozzle is attached with jet nebulizer. Typically, 0.25 M of aqueous copper chloride ($CuCl_2.2H_2O$, Sigma Aldrich) was used as coating solution and the films were prepared onto glass substrate mounted on a heater plate at 300°C. In this present work, the coating thickness was controlled by varying the precursor volume (10, 20, 30 and 40 ml). The rate of spray coating is 0.75 ml/min; therefore spray cycle duration is extended with larger precursor volume. The CuO aerosol generated from nebulizer undergoes successive pyrolysis due to the temperature gradient between substrate (300 °C) and nozzle gun and finally CuO is decomposed on the substrate as follows:

$$CuCl_2 + H_2O \rightarrow CuO + 2HCl \qquad (1)$$

The thickness of the resultant electrodes for different volume of spray solution coating is measured by stylus profilometer and found to be 0.58, 1.23, 2.59 and 3.07 micron, respectively. For the sake of discussion, the samples name were coined as *CuO-x* (x=10, 20, 30 and 40), here x denotes the volume of precursor solution in ml.




**Scheme 1.** Illustration of jet nebulizer spray pyrolysis system using pocket-size medical nebulizer (inset: photo of nebulizer) used for CuO coating.

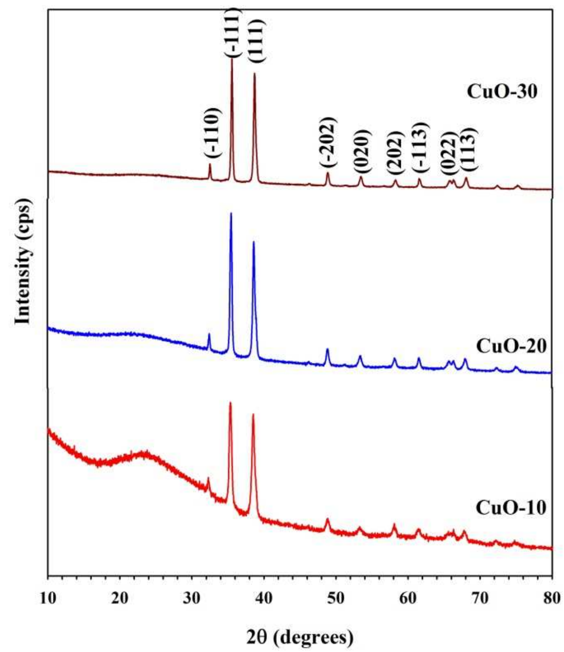



**Figure 1.** XRD results of nebulizer spray coated films for different volume of Cu precursor solution.

The crystallite structure of the resultant CuO coatings was studied with X-ray spectrometer (Rigaku Denki Japan) using CuKα radiation. A Field Emission Scanning Electron Microscope (FE-SEM, JEOL, JSM-7600F) was used to observe the microstructures of the coatings. The surface roughness of the coatings was evaluated by laser microscopy (KEYENCE, VK-X200 series). The static water contact angle was measured using contact angle meter (KYOWA, model DM-301). At least five measurements on different positions were carried out and the average value is presented as final contact angle value. A water drop (~ 5 µl) was placed on the coating surface for approximately 10 sec to achieve equilibrium position. A Canon Digital Camera (G 15 series) was used to capture the optical images. A self-cleaning performance was observed by spreading carbon black dust particles on the superhydrophobic coating and collected by rolling water drops. A stable wetting property of superhydrophobic coating was confirmed by impacting high speed water jet on overall coating surface. A water jet was created by applying normal force to a syringe.

The XRD results of *j-NS* coated films for different precursor volume are presented in Fig. 1. The predominant peak shoulders at $2\theta = 35.2°$ and 38.4° corresponds to the (-111) and (111) crystallite phase of monoclinic CuO (JCPDS-80-1916).[9e, 14] The small peaks observed at $2\theta = 32.4°$, 48.7°, 53.2°, 57.8°, 61.4°, 65.4° and 67.8° are attributed to (-110), (-202), (020), (-113), (022) and (113) crystallite phases, receptively. The width of (111) crystallite peak gradually decreases with increasing volume of spray solution, which clearly indicates the crystallite growth. The average grain size of the CuO films were estimated using Scherrer's relation[15] and found to be 21.4, 28.2 and 37.9 nm, for CuO-10, CuO-20 and CuO-30 samples, respectively. The surface morphologies of the *j-NS* coated CuO samples are presented in Fig.2 (a-h). Comparing the Figs. 2(b), 2 (d), 2(f) and 2(h), the

CuO grain size was found to increase with spray cycle duration. In addition, the spherical shape of CuO nanoscopic grains at CuO-10 was drastically transformed to anisotropic grains (Fig.2h, CuO-30) by increasing spray coating duration. This clearly demonstrates that the mist-type aerosol distribution by jet nebulizer modifies the successive crystallite growth of each layer. Unlike pneumatic spray pyrolysis technique, there is no film peel-off or particle coagulation effect observed even at long duration coating (~ 30 min). This corroborates that *j-NS* is feasible for robust coatings through fine tuning the aerosol droplet distribution on the substrate. The grain size enhancement from CuO-10 to CuO-30 is consistence with XRD results (peak sharpening at (111) crystallite phase). In view of crystallite texture, the CuO-30 sample shows denser growth with rough interstices compare to less spray cycle coatings (CuO-10 and CuO-20). With further increase in the spray coating cycles, the recrystallization process takes place which leads to large voids on the surface. The root-mean-square (RMS) of surface roughness was measured and found to amend from 50, 60, 150 and 230 nm for C-10, C-20, C-30 and C-40 coatings, respectively. It is anticipated that CuO-30 sample may exhibit better superhydrophobic behaviour than other samples owing to its higher surface roughness and denser growth which may block the air packets.

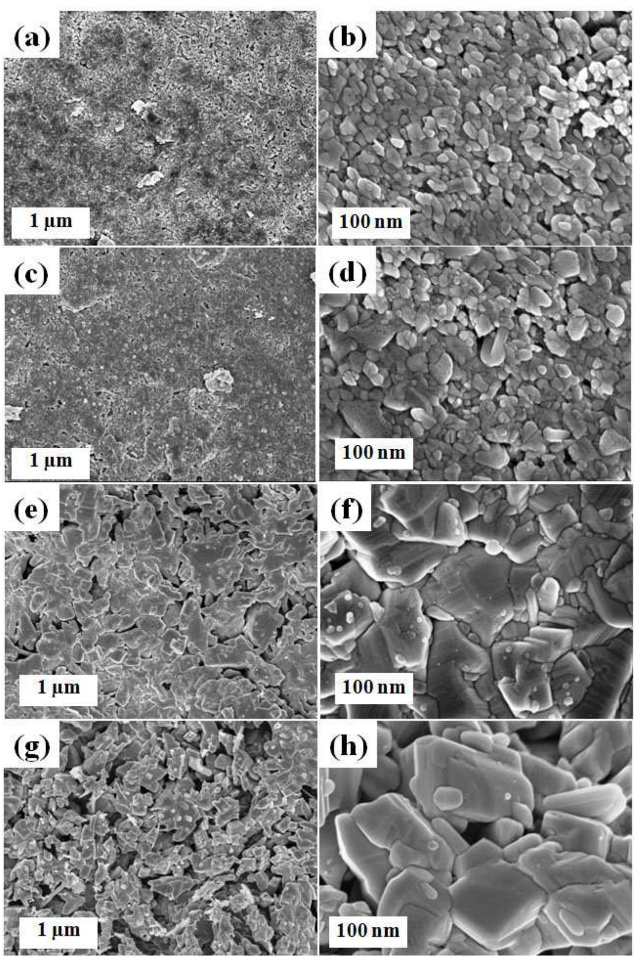



**Figure 2.** SEM images of *j-NS* coated CuO samples on glass substrate (a) C-10 (c) C-20 (e) C-30 and (g) C-40 (high magnification at 100 nm scale is presented on the right hand side of the corresponding images).

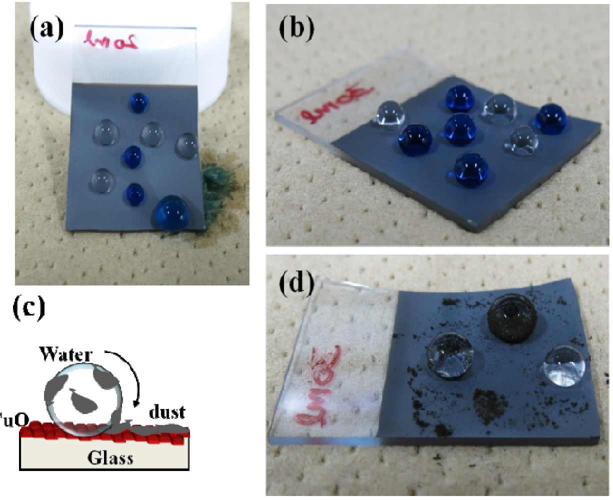



**Figure 3.** Photograph of water droplets on (a) CuO-20 and (b) CuO-30 surface; (c) schematic illustration of superhydrophobic self-cleaning coating; (d) carbon dust particle are self-cleaned on superhydrophobic CuO-30 surface.

The C-10 and C-20 coatings showed microscopically smooth morphology composed of closely packed nanoscopic grains (Fig.2b and 2d). The contact angles of different CuO coatings were presented in **supporting information table S1**. A water drop placed on C-10 and C-20 coatings acquire almost hemispherical shape with nearly similar contact angles of 130° and 134°, respectively. The water drops were in Wenzel's wetting state and therefore the adhesion between water drop and the CuO surface was very strong. As shown in **Fig. 3 a**, the water drops sticks to the coating surface (C-20) even after the surface was sloped at 50° and remained adhered to surface with more than 90° tilting. The similar wetting properties were observed in the case of C-10 coating. The surface roughness of the coatings was not adequate to trap air pockets inside the interstices and therefore a water drop intrudes and wets the surface structure displaying a sticky high adhesion. The highly adhesive Wenzel's wetting state of *j-NS* coated CuO was transformed into low adhesive Cassie-Baxter's wetting state in case of C-30 coatings. **Fig. 3b** depicts the photograph of the water drops on C-30 coating surface. Some of the water drops were blue coloured using methylene blue (MB) for clear visibility of the water drops. All the water drops placed at different locations on the coating surface acquired perfect spherical shape confirming the uniformity of the *j-NS* coating. As a result of larger grain size with rough surface morphology, the C-30 sample exhibits superhydrophobic behaviour. The water drops on this sample exhibited a contact angle of 154° and quickly rolled off the surface even under small disturbance. The air pockets get trapped in the rough interstices and as a result the water drops sit on the air layer and eventually rolls off the surface. This extreme low adhesion between the water drops and the coating surface represents Cassie-Baxter wetting state. However, in the case of C-40 coatings, the surface microstructure showed rough morphology as well as increased surface roughness; the apparent voids between the grains were observed. Though, the air pockets formed in these voids, they were pinched out and water get intrude in the microstructure. As a result, the coating showed a decrease in water contact angle of 125°, exhibiting strongly adhesive Wenzel's wetting state. From the above discussion, it demonstrated that superhydrophobicity of the CuO coatings may stemming from the combined effect of surface roughness and deoxidation of the CuO surface in air. The air pockets remained trapped in the interstices which does not allow water drop to percolate inside the rough structure.

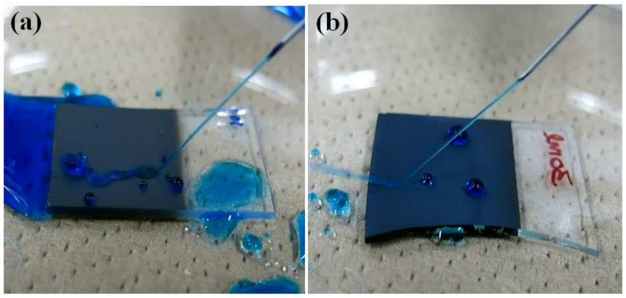



**Figure 4**. Photograph of water jet impact on (a) CuO-10 and (b) CuO-30 surface.

The Fig. 3c illustrates the schematic of self-cleaning phenomena on superhydrophobic surface. A moving spherical water drop tucks up all the dust particles accumulated on the superhydrophobic surface and subsequently self-cleaning the surface. A self-cleaning behaviour of superhydrophobic CuO surface (C-30) was presented in Fig. 3d. A water drop was gently placed on copiously and uniformly spread carbon black powder and rolled slowly to collect the dust particles. The adhesion between water drop and dust particles was higher than the adhesion between dust and superhydrophobic solid surface. The three water drops on the superhydrophobic CuO surface represents heavily wrapped by the dust particles with fresh water drop. A little tilting motivates the dust particles wrapped water drops to roll off the surface. Thus by using approximately 8-10 water drops, the superhydrophobic CuO surface (2.5 x 2.5 $cm^2$) can be made dust free, exhibiting its excellent self-cleaning behaviour.

Superhydrophobic surfaces may lose their excellent wetting properties (static as well as dynamic) and make transition from non-sticky Cassie-Baxter's to sticky Wenzel's wetting state by the impact of high speed water jet. In our previous report, we showed the effect of water jet impact on the wetting properties of superhydrophobic coating.[16] It is realized that the water jet strongly impinge on the chemical treated superhydrophobic surface and weaker surface mostly lose their wetting property.[17] Therefore, we analyze the wetting stability of CuO surface against water jet. The Fig. 4 shows the water jet impact study performed on C-20 and C-30 coating surface. As depicted in **Fig. 4a**, the high speed water jet hits the C-20 coating surface and the water get accumulated at the point of impact. A high speed water jet impinges into the coating surface and wets it due to lack of air pockets in the interstices. However, as shown in **Fig. 4b**, water jet strike on the C-30 coating surface and eventually bounce off the surface, leaving no water residue behind. The abundant amount of air pockets present inside the rough structure opposes the high speed water jet to enter into the coating structure; as a result water jet was bounced off straightaway. However, the water jet was kept bouncing off for impacting water jet at same position for 60 sec. The water jet was moved over entire surface and finally checked the wetting properties of the C-30 coating surface, which show no loss in static as well as dynamic water contact angle. A stable Cassie-Baxter superhydrophobic wetting state was maintained after high speed water jet impact. The observed self cleaning property with robust superhydrophobic nature of CuO-30 can be extended to other surfaces. The optimized superhydrophobic CuO on glass substrate can be transformed onto metal mesh that may effectively perform as oil-water separation membranes,[18] and is now in progress. Further work will focus on developing robust coatings with polymer-CuO mixtures using *j-NS* method, which will be futuristic candidate in wetting switches (superhydrophobic to hydrophilic and vice versa). However, these coating on low temperature withstanding substrates such as polymer and plastic were finds inadequate due to the high temperature processing.

In summary, a robust superhydrophobic CuO coating was achieved by custom-made jet nebulizer spray coating technique. The water drop displayed non-wetting Cassie-Baxter state on CuO-30 surface. The spray coated superhydrophobic CuO surface exhibited excellent self-cleaning property. A stable Cassie-Baxter superhydrophobic wetting state was maintained even after high speed water jet impact. Our scientific findings of rapid and robust superhydrophobic CuO coatings on glass substrate using custom-made jet nebulizer spray favours large scale coating at very low-cost over a wide range of high temperature processing substrates.

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## Notes and references

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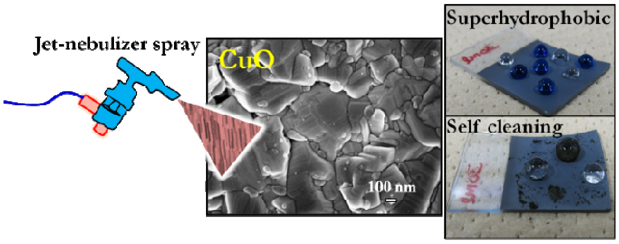
**Table of Content**




Pocket-size nebulizer equipped jet-spray coating of monoclinic CuO crystallite surface showed excellent superhydrophobic self-cleaning property owing to their compact crystallite texture and high surface roughness.