This chapter describes the superhydrophobic property of Teflon coated and bare hetero-nanostructures ZnO-Cu₂O samples for impinging droplet. Two step (a) anodic etching and (b) solution bath deposition were used to grow the ZnO-Cu₂O hetero-nanostructures and subsequently hydrophobized using OTS-SAM and Teflon AF. XRD and FE-SEM were used for phase and morphology characterizations, respectively. These surfaces were characterized for static contact angle and studied dynamics of impinging droplet. Teflon covered ZnO-Cu₂O hetero-nanostructures shows ultrahigh static contact angle (CA) of about 173° and exhibits droplet bouncing up to Weber number \( W_e \sim 72 \). The bare surface (CA \( \sim 150^\circ \)) however shows bouncing for \( W_e < 30 \) and sticking when \( W_e \geq 30 \).
6.1 Introduction:

Natural superhydrophobicity and self cleaning is an inherent property of Lotus leaves due to its intrinsic hierarchical surface structure and epicuticular wax secreted by itself.\cite{1} Inspired from “lotus effect” scientist community have made lot of successful efforts to realize artificial superhydrophobic surfaces.\cite{2} There is an enormous literature that describes research on studying of rough surface design and its wettability.\cite{3} In fact, 1D nanostructures of diverse materials is used for designing hierarchical 3D surface structure which is favourable for typical roughness required for hydrophobicity.\cite{4} Most reports are on rough polymer surfaces,\cite{5} TiO$_2$ nanostructured films,\cite{6} etched or metal deposited silicon surfaces with micro/nanostructures,\cite{7} and carbon nanotubes (CNTs) surfaces.\cite{8} Most of the work is focussed on functionalisation of 1D or 2D nanostructures by low surface energy materials to attain desired superhydrophobicity,\cite{9} but a modest work on the metal oxides heterojunction nanostructures functional for self cleaning phenomenon.\cite{10} Recently, hetero-nanostructures oxides with multiscale roughness received more attention for self cleaning applications.\cite{11} Because of uniqueness in multiscale structures exhibits large surface area with full of air pockets increases effective area fraction and impede the transition from Cassie-Baxter\cite{12} to the Wenzel state\cite{13} and improve the morphological stability of a liquid droplet. Nosonovsky and Bhushan suggested that destabilizing factors responsible for such a transition have different characteristic length scales, and thus, multiscale (hierarchical) roughness plays an important role in stabilizing the composite interface.\cite{14} In addition to multiscale roughness, one important property is the ability of a water droplet to bounce off a surface is crucial for designing thermodynamically stable superhydrophobic surfaces. When a droplet hits a surface, it can perform different characteristics properties such as deposition/sticking, rebound, and fragmentation depending on surface conditions.\cite{15} There is an important aspect of studying droplet impact on solid surfaces (planar, structured, hydrophobic, hydrophilic) and post analysis like spreading dynamics, bouncing and jetting properties as a function of impact velocity and ambient pressure. Lohse and coworkers have investigated these aspects in greater detail.\cite{16} Nevertheless, the robustness and longevity of the modified surfaces still pose major challenges for the overall development of superhydrophobic surfaces to be used in harsh environmental applications.
In this context, out of semiconducting oxides, Zinc Oxide (ZnO) is well-known metal oxide n-type semiconductor because it is easy to produce various nanostructures by simple bottom-up techniques. It is straightforward to grow 1D nanostructures of ZnO and versatile for convert into desired morphologies. Due to their uniqueness in structures they have promising applications in the field of waterproof electronic devices. Also Cuprous Oxide (Cu₂O) is one of the stable metal oxide semiconductors, earth abundant material, but very less explored in metal oxides heterostructure nanomaterials for superhydrophilic applications. Guo et al. have demonstrated superhydrophobic property and droplet bouncing on a hierarchical SAM covered CuO-ZnO hetero-nanostructures surface. Functionalized surface shows water contact angle of nearly 165° and droplet bouncing in limited range of impact velocity. The droplet impact on superhydrophobic material is the most reliable test for sustainable water repellency. This is also called as dynamic wetting. During the droplet impingement on a structured surface the forces acting on the droplets that are responsible for overcoming any barrier if exists. The kinetic energy per unit volume i.e. pressure carried by the droplet is given by

\[ P_d = \frac{\rho v^2}{2} \]  \hspace{1cm} (6.1)

where, \( \rho \) is density of water and \( v \) is speed.

The Laplaces pressure due to characteristic structure can be given by

\[ P_L = \gamma \left[ \frac{1}{R_1} + \frac{1}{R_2} \right] \]  \hspace{1cm} (6.2)

where, \( \gamma \) is interfacial tension and \( R_1 \) and \( R_2 \) are the principal radii of curvature. Droplet impinging with high enough speed may overcome \( P_L \) and wet the surface so called Cassie-Baxter to Wenzel transition. Stability of the droplet in this new equilibrium state is mainly depends on the local wetting (intrinsic contact angle to the surface). For instances hydrophilic planar surfaces shows complete wetting/spreading of drop in this state, on the other hand droplet may shows dewetting in case of hydrophobic surface. This is precisely a of reversible Cassie-Wenzel transition which is of current interest in many technological applications.

In this work, we account the growth of hierarchical ZnO-Cu₂O hetero-nanostructures through open aqueous solution combined with anodization of copper surface. This surface is further modified by OTS self assembled monolayer and amorphous fluoropolymer Teflon AF 1600. These surfaces are studied for static and dynamic
superhydrophobicity (SH) via impinging droplet. Teflon covered shows ultrahigh CA along with droplet bouncing at considerable large range of impact velocity. On the other hand bare surface shows droplet bouncing for limited velocities. Our study demonstrates importance of multi-scaled roughness via hierarchical growth of nanometer ZnO on micrometer needles along with Teflon coating that exhibits excellent SH for self cleaning applications.

6.2 Experimental Techniques:

The Cu$_2$O nanoneedles film was grown directly on copper substrate employing a protocol previously reported by us.$^{[21]}$ In brief, Cu$_2$O nanoneedles on copper surface were grown by anodization technique in conventional two electrode cell in of KOH electrolyte at 2 molar concentrations. Electric current was passed through a copper plate with graphite counter electrode. Process parameters were optimized and reported elsewhere.$^{[21]}$ It is known that anodization process forms evenly spaced Cu(OH)$_2$ nanoneedles film on the substrate. Samples were rinsed thoroughly with Millipore Milli-Q water and dried in vacuum and characterized for water contact angle (WCA) which was about $\sim$ 0° i.e. hydrophilic nature possibility due to Cu(OH)$_2$. These substrates were then annealed at 450 °C in controlled oxygen pressure of $5\times10^{-5}$ mbar for oxide formation. Such surface was again characterized for wetting remarkably showing WCA of about 143°. In the second stage of the growth, seed assisted growth of ZnO nanorods on Cu$_2$O nanoneedles surface was carried out. On the surface of these Cu$_2$O nanoneedles, a seed layer of ZnO was deposited by dip coating technique. Initially seed suspension was prepared using 5 mM Zinc acetate in ethanol. Films were again annealed in vacuum ($5\times10^{-5}$ mbar) at 250 °C to forms ZnO nucleating sites on a parent Cu$_2$O needle. For the facile growth of ZnO nanorods on Cu$_2$O needles, an equimolar (25 mM) solution of Zn(NO$_3$)$_2$, hexamethylene tetramine (HMT) was used as precursor and carried out at 95 °C using open aqueous solution deposition technique at constant mechanical stirring for 15 minutes time duration. This deposition process was also optimized for concentration and deposition and reported by us. Samples were further rinsed with Milli Q water and dried in dry nitrogen. In the last ZnO-Cu$_2$O samples were again annealed in vacuum ($5\times10^{-5}$ mbar) at 250 °C for better adherence and crystallinity of the ZnO nanorods on Cu$_2$O needles. These deposition conditions for Cu$_2$O phase and ZnO morphology are systematically
optimized and results were published elsewhere. This surface was hydrophobized by Octatrichlorosilane (OTS) self assembled monolayer (SAM) in Toluene solution followed by rinsing several times using Toluene. Another batch of samples were hydrophobized using a nm thick layer of amorphous fluoropolymer Teflon AF using conventional dip coating method. In brief, 3 wt. % solution of amorphous fluoropolymer Teflon AF (1600) (DuPont) in perfluorinated solvent FC 75 (3M) was used for coating at speed of 20 cm/min and subsequently dried in laminar flow for 30 min. Finally samples were heated at 110 °C in vacuum oven for 1 hour the removal of solvent and slowly cooled to room temperature.

6.3 Characterization Techniques:

Various characterization techniques such as X-ray diffraction (XRD, Philips X’Pert PRO), Field Emission Scanning Electron Microscopy (FE-SEM, Hitachi S4800) were used for characterization of phase and morphology, respectively. Wetting property was studied extensively using contact angle goniometry, OCA20 system equipped with high light transmitting capacity CCD camera and dosing system. Images were analyzed using SCA 20 software (OCA 20 and software both from dataphysics, Germany). A contact angle hysteresis (CAH) was analyzed by tilting a base with simultaneous CA measurement and roll-off angles. The wetting and bouncing of the impinging droplet on sample was carried out using high speed imaging. In details Millipore Milli-Q water droplet was released from a precision needle (Teflon AF coated precision needle with OD 0.91 mm) from heights between 1 to 30 cm and droplet impinging velocity was varied. Droplet volume was also controlled with the help of syringe pump (Harvard, pico plus). The dynamics of the droplet landing and subsequent bouncing behavior was captured using high speed camera operating at 177 frames per second (FPS). The images are analyzed using ImageJ [ref. http://rsb.info.nih.gov/ij/], open source software. Kinetic energy (velocity of descent) of the impinging drop was varied by releasing a droplet from different heights. All measurements were conducted in a condition 22±1 °C and 45±5 % relative humidity (RH). Furthermore, droplets of Milli-Q water 9 μL were used to estimate the static contact angle. Each contact angle was measured repeatedly more than ten times at the different places on the sample and statistics was presented. The sets of samples viz. bare ZnO-Cu2O, OTS self Assembled Monolayer (SAM), covered films and Teflon AF covered films was characterized for water drop bouncing in detailed.
6.4 Results and Discussion:

6.4.1 Structural and Morphological Studies:

The surface morphology and structure of bare and Teflon modified samples were studied using Field Emission Scanning Electron Microscopy (FE-SEM) and X-Ray Diffraction (XRD) techniques respectively. Figure 6.1(a) shows low magnification FE-SEM images taken at different magnifications. Grass like morphology with dense nanoneedles growth is observed with needle diameter varies between 50 to 100 nm and 5 to 9 μm in lengths. This morphology provides template for secondary ZnO growth. Figure 6.1 (b) shows the low magnification morphology and (c) presents high resolution FESEM image after the secondary ZnO growth. The ZnO growth conditions like concentrations and deposition time were critically optimized and discussed in detail in ref. [21]. Here growth takes place in the form of dense nanorods enclosing the entire surface of needles. Uniform covering of ZnO on primary nanoneedles forms excellent hetero-nanostructures morphology. A length of single nanorod is about 700-800 nm whereas diameters varies between 40-50 nm. Notably, this secondary growth creates self similar multiscale structure which is of interest in context to hierarchical roughness. These samples are characterized for the phase identification as shown in Fig. 6.1(d). XRD clearly shows polycrystalline Cu$_2$O and Wurtzite ZnO phase. Mix phase of copper oxides like CuO are not seen. X-ray also indicates the diffraction from different Miller indices indicating a non-epitaxial growth of ZnO on Cu$_2$O needles.

Owing to the unique surface morphology of ZnO-Cu$_2$O hetero-nanostructures, it is mainly explored for perpetual superhydrophobicity applications. To mimic a low surface energy wax layer secreted on Lotus leaves, our samples were covered with OTS-SAM and Teflon AF layer. The concentration of the Teflon AF solution and dipping speed was optimized to preserve multiscaled roughness.
Figure 6.1: Low resolution FE-SEM image of (a) Cu$_2$O nanoneedles (b) ZnO-Cu$_2$O hetero-nanostructures. (c) High resolution FE-SEM image of ZnO-Cu$_2$O hetero-nanostructures. (d) X-Ray Diffraction pattern of ZnO-Cu$_2$O hetero-nanostructures. * represents copper substrate peaks.

Figure 6.2 (a), (c), (e), (g) and shows FE-SEM of a bare samples and Fig. 6.2 (b), (d), (f) and (h) for Teflon coated samples. SEM images clearly shows ZnO-Cu$_2$O hetero-nanostructures of bare and Teflon AF coated in low and high magnification. It confirms the multiscale surface topology in both samples. A Teflon layer thickness on a ZnO-Cu$_2$O surface is estimated indirectly by performing a coating on plane surface which is about 10 nm. From high magnification scale it is clearly seen contrast between the images of Teflon coated and bare ZnO-Cu$_2$O samples. The thickness of the samples are further explored for static contact angle measurements and droplet bouncing events under a range of parameter space like impact velocity or dimensionless Weber number $W_e$, a ratio of kinetic energy to surface energy per unit area.
Figure 6.2: SEM images (a) (c) (e) and (g) represents all surface morphology of bare Cu₂O-ZnO hetero-nanostructures and (b), (d), (f) and (h) are the corresponding images of Teflon modified hetero-nanostructures surface.
6.4.2 Water Contact Angle Analysis:

Figure 6.3 shows a plot of steady state water contact angle on bare, OTS-SAM and Teflon coated ZnO-Cu$_2$O nano-heterostructure surface. Water CAs on Cu$_2$O surface i.e. before secondary growth of ZnO is also shown in the same plot. Affectively increase in CA of about 10° is seen in case of bare and OTS-SAM covers surface while 20° increase is seen in case of Teflon coated surface. Thus secondary ZnO growth has significance in nanoscale hierarchical surface roughness. WCA on Teflon coated ZnO-Cu$_2$O surface is about 173° ± 3° which is highest amongst all samples. Contact angle hysteresis (CAH) and roll-off angle which is found to be about 5°. Bare and OTS-SAM covered surfaces have contact angles in the range of 150° ± 3° with CAH and roll-off angles are in a rage 10-30°. ZnO-Cu$_2$O bare surface and OTS-SAM covered surfaces shows identical CAs and CAH; we subsequently characterized bare samples and compared the results with Teflon coated samples.

Figure 6.3: Statistical distribution of static contact angle measured on 10 different locations for each sample.

We attempted to model a wetting of water drop on a bare surface of ZnO-Cu$_2$O and Teflon coated surface. Schematic shows a water drop resting on ZnO-Cu$_2$O surface [Fig. 6.4 (a)] and on Teflon coated surface [Fig. 6.4 (b)]. A large difference in CA, about 20°, in case Teflon coated samples is observed which can be explained on the
using Cassie-Baxter equation, as given as (Eq.6.3)

\[
\cos \theta^* = r_f f (\cos \theta_f + 1) - 1
\]  

(6.3)

where \( \theta^* \) is an apparent CA, \( r_f \) is roughness ratio, \( f \) being area fraction and \( \theta_f \) is an intrinsic CA on plane surface. Here WCA on plane Teflon AF surface is about \( 110^0 \)\(^\text{[23]} \) on the other hand plane ZnO surface is hydrophilic (CA < 90), a significant change in the \( \theta_f \) value occurs although roughness ratio, area fraction etc. approximately remains same.

Figure 6.4: Schematic shows water drop on multiscaled hetero-nanostructures (a) ZnO-Cu\(_2\)O and (b) Teflon coated surface. Water drop remains in the Cassie-Baxter “Fakir” state a fraction of drop base stays on air cushion and supported on ZnO nanoneedles.

Teflon coated surface exhibits a superhydrophobic property satisfying Cassie-Baxter criterion. This quasi-equilibrium state can stabilize to a stable equilibrium Wenzel state with an external stimuli like mechanical vibration\(^\text{[24]} \), Electrowetting induced\(^\text{[25]} \), drop impact \(^\text{[26]} \) etc. Superhydrophobicity exhibited by these surfaces is tested for impinging droplet which possibly leads to bouncing of droplet via reversible Cassie-Wenzel state or remain sticky Wenzel state. Subsequent section deals the same in detail.

**6.4.3 Drop Impact Characteristics:**

Water droplet of controlled volume is realized from definite height on to substrate, Teflon coated and bare ZnO-Cu\(_2\)O, at different impinging velocity or Weber number. The Weber number, \((\text{We} = \rho V^2 R/\gamma)\), is a ratio of kinetic to surface energy of incoming droplet determines deformability of the droplet, where \( \rho \) and \( \gamma \) are the water density and surface tension, respectively. Also dimensionless parameters are associated with drop impact characteristics is Reynolds number \( \text{Re} \) (\( \text{Re} = \rho V R/\mu \)) which is defined as the ratio of inertial forces to viscous dissipative forces, where \( \mu \) is viscosity of water.
On a place surface kinetic energy act against the surface energy in deforming the droplet at impact event, however on multiscaled rough surfaces, kinetic energy is used

\[ We = 35.93 \]

\[ We = 39.49 \]

\[ We = 46.67 \]

\[ We = 50.26 \]

\[ We = 53.85 \]

\[ We = 71.81 \]

*Figure 6.5:* Snapshots of a water droplet hitting on two different hetero-nanostructures surface viz (a) bare ZnO-Cu₂O surfaces (b) Teflon modified ZnO-Cu₂O surfaces. (Color in red shows droplet events on Teflon coated surface at different time instants). Droplet bounces off from the surface for range of Weber number.

in Cassie-Wenzel transition and then spreading. Cassie-Wenzel is more stable equilibrium state of the drop therefore droplet can stabilize in this state. Equal and
opposite momentum on a droplet may bring it again to Cassie state by overcoming wetting force. This aspect provides a sustainability of the superhydrophobicity upon droplet impact.

Impacts events on Teflon coated and bare ZnO-Cu$_2$O surface is recorded using high speed camera, some of the representative images are shown Fig. 6.5. Weber number is ranges from 5 to 72. On a bare surface, droplet bouncing is seen only for low $We$, and sticking of droplet is seen when droplet impinging above threshold $We$. Interestingly on the Teflon coated surface, droplet bouncing is seen from low to considerably high $We$ ($\sim 72$). In the present case, limit on values of $We$ is mainly due to experimental constraints and CCD camera frame rate.

### 6.4.4 Droplet Impact Phase Diagram:

Within a parameter space mainly $We$ and bouncing events phase diagram can be drawn to highlight regimes of stable bouncing and sticking. Figure 6.6 shows the bouncing-sticking phase diagram.

*Figure 6.6: Morphology phase diagram highlighting regimes of stable bouncing and sticking on Teflon covered and bare ZnO-Cu$_2$O surface, respectively.*
The continued bouncing of droplet on Teflon covered ZnO-Cu$_2$O samples shows a dramatic difference in state of a droplet when it goes to Wenzel state via impact kinetic energy. Droplet states on both substrates can be illustrates using schematic Figures 6.7 (a) and (b).

Figure 6.7 Schematics illustrating a transition from Cassie-Baxter to Wenzel state after a threshold impact or $We \geq 30$ on bare substrate. (b) Water droplet impacting directly on to hydrophobic, non wetting Teflon surface leading to bouncing for considerably large rage of $We$.

If incoming droplet has a sufficient energy to overcome Cassie-Wenzel state then it preferably goes to new stable Wenzel by smashing air cushions which makes a direct contact of water on nano-structured surface as shown in schematic. This is experimentally observed as can be seen from drastic decreases in CA from 140$^\circ$ to 70$^\circ$. Water impregnates a texture leading to stronger adhesive force with surface. An excess energy would dissipate to retract drop from wetted surface that acts against substrate-liquid adhesive forces. This adhesive force mainly depends on the local microstructure and capillarity. In case of the Teflon coated surface a major difference is in local subsurface energy i.e. water-Teflon CA. Teflon coating coves a ZnO-Cu$_2$O therefore hydrophilic ZnO surface becomes hydrophobic with CA about 110$^\circ$. Droplet upon impact with sufficient kinetic energy does not leave the droplet to remain invaded in the ZnO nano-structure, lead to bouncing in for wide range of $We$. This property of a Teflon coated surface is further used for self cleaning applications.
6.4.5 Application in Self Cleaning:

Self cleaning behaviour of Teflon coated ZnO-Cu$_2$O multiscale nanostructured surface is investigated to demonstrate a proof of principle. Figure 6.8 shows snapshots of the images demonstrating self cleaning property. As seen in the figure, chalk dust particles are placed on the surface. A 9 $\mu$l water drop from a precision syringe tip is brought in contact with surface as shown. The needle along with a droplet is moved from left to right and back (direction is shown by blue arrow). Indeed, high CA is also seen in Figure. The water droplet remains intact without any apparent deformation, preserving a solid ball while sliding on a smooth surface. Excitedly, the dust particles entered into the droplet and accompanied with the sliding of droplet without any dust particles remained. These results demonstrate that Teflon coated ZnO-Cu$_2$O multiscale hetero-nanostructured surface demonstrates a self-cleaning performance.

![Figure 6.8: Snapshots of droplets showing self-cleaning behaviour for ZnO-Cu$_2$O hetero-nanostructured array. A 2 mm water droplet slides (not rolls off) the surfaces taking away dust on the surface.](image-url)
6.5 Conclusion:

We report a growth of heterostructured ZnO–Cu$_2$O surface using two step processes. XRD confirms that crystalline phase of ZnO grown on a single phase Cu$_2$O which exhibits multiscale nano-micro morphology as seen in the FE-SEM. The surface is further coated using Teflon AF, which shows excellent superhydrophobic property with WCA of about 173$^\circ$, while bare surface has WCA of about 150$^\circ$. Moreover continued droplet bouncing is observed up to a limit of high $We \sim$72. On the other hand, bare surface exhibits droplet bouncing over limited range of $We$ ($We < 30$). Teflon coated surface demonstrates an excellent superhydrophobicity along with a self cleaning property.
References:


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