Fabrication of Superhydrophobic Copper Surface on Various Substrates for Roll-off, Self-Cleaning, and Water/Oil Separation

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Ⓢ Supporting Information

ABSTRACT: Superhydrophobic surfaces prevent percolation of water droplets and thus render roll-off, self-cleaning, corrosion protection, etc., which find day-to-day and industrial applications. In this work, we developed a facile, cost-effective, and free-standing method for direct fabrication of copper nanoparticles to engender superhydrophobicity for various flat and irregular surfaces such as glass, transparency sheet (plastic), cotton wool, textile, and silicon substrates. The fabrication of as-prepared superhydrophobic surfaces was accomplished using a simple chemical reduction of copper acetate by hydrazine hydrate at room temperature. The surface morphological studies demonstrate that the as-prepared surfaces are rough and display

superhydrophobic character on wetting due to generation of air pockets (The Cassie−Baxter state). Because of the low adhesion of water droplets on the as-prepared surfaces, the surfaces exhibited not only high water contact angle (164 ± 2°, 5 μL droplets) but also superb roll-off and self-cleaning properties. Superhydrophobic copper nanoparticle coated glass surface uniquely withstands water (10 min), mild alkali (5 min in saturated aqueous $NaHCO_3$ of pH ≈ 9), acids (10 s in dilute HNO_3, H_2SO_4 of pH ≈ 5) and thiol (10 s in neat 1-octanethiol) at room temperature (25−35 °C). Again as-prepared surface (cotton wool) was also found to be very effective for water−kerosene separation due to its superhydrophobic and oleophilic character. Additionally, the superhydrophobic copper nanoparticle (deposited on glass surface) was found to exhibit antibacterial activity against both Gram-negative and Gram-positive bacteria.

KEYWORDS: superhydrophobicity, copper, contact angle, roll-off, self-cleaning, kerosene-water separation

■ INTRODUCTION

Wettability and adhesiveness phenomenon of water, owing to the interactions between liquids and solid surfaces on hydrophobic and hydrophilic surfaces, has been found to lead innumerable applications in our life.[1,2] Explicitly, superhydrophobic surfaces have attracted prodigious attention due to their wide array of applications in the fields of self-cleaning, anti-icing, antibiofouling, drug delivery, anticorrosion, textiles, antifreezing etc.[3−8] These surfaces show the water contact angles (WCAs) greater than 150° and low contact angle hysteresis (<5°). The phenomenon of superhydrophobicity has been explained by two renowned theories proposed by Wenzel[9] and Cassie[10] independently. Wenzel theory explains that complete wetting of rough surface by water droplet results in the contact angles due to the surface roughness. The water droplet sticks to the surface, and thus the Wenzel state displays very high adhesive property. On the other hand, Cassie theory elucidates that water droplet wets the surface, partially developing the air pockets between the water droplet and surface. So in this case, water droplet does not penetrate inside the rough surface region, but it just rests on top of asperities of surface. The Cassie state of wetting provides large WCAs having low contact angle hysteresis and thus results in a roll-off superhydrophobic surface. So the Cassie state exhibits

low adhesive property. Low adhesive superhydrophobic surface renders the rolling-off property of water droplets due to the surface roughness of low energy materials, whereas the high adhesive superhydrophobic surface causes the pinning of water droplets on the surface as a result of surface roughness.[11−14] It is noteworthy to mention that roll-off behavior of superhydrophobic surface has useful application in self-cleaning.[15] However, superhydrophobic and superoleophilic materials have also been exploited for oil/water separation.[16] On the other hand, the high adhesive superhydrophobic surface has also become impressive for their imperative applications on microfluidic systems, biochemical separation, etc.[13,17]

Inspired by the potential application of superhydrophobic surfaces, many researchers made successful fabrication of these surfaces by electrodeposition,[18] electrospinning,[19] anodization,[20] laser treating,[21] etc. with complexity. These also have been fabricated through plasma treatment, templation, lithography, chemical deposition, etc.[22] However, all these methods have certain limitations such as tedious fabrication, severe condition,

expensive materials, poor durability, etc.[23] In the past decade nanoscience has captured gigantic attention due to its wide array of applications. Consequently, it has been applied to fabricate superhydrophobic surfaces to triumph over aforementioned limitations. More importantly, researchers have paid attention on the hierarchy and micro/nano scale rough surfaces. For examples, our synthesized hierarchical superhydrophobic ZnO hollow spheroids and nanoflowers are worth mentioning.[24,25] Deng et al. reported the fabrication of superhydrophobic alumina surfaces.[26] Recently, superhydrophobic poly(methyl methacrylate) nanotube array surface has been developed by Wang et al.[27] Fluorinated raspberry-like polymer surface for superhydophobicity,[28] superhydrophobic polymer carbon nanocomposite,[29] and superhydrophobic carbon nanotube array surface has also been fabricated.[30] On the other hand, superhydrophobic cotton,[31] textile,[32] and Teflon surfaces[33] have also been fabricated for the industrial interest.

Copper, an important engineering material, has been extensively used in the industrial field[34] and so forth in the past few years; researchers have discovered many methods to fabricate superhydrophobic copper surfaces beating the above-mentioned dilemma also. For examples, superhydrophobic s ilver film on copper substrate,[35] superhydrophobic CuO film,[36] honeycomb-like three-dimensional porous structures of super-hydrophobic hydroxy cupric phosphate heptahydrate fabricated copper surface,[37] etc. have been described. The fabrication of Cu with CuO surfaces,[38,39] fluorinated Cu surface,[40] thiol-decorated Cu surface,[41] Cu nanowires with $Cu(OH)_2$ surfaces,[42] Cu foams,[43] and copper tubes[44] have also been reported. But the preparation of superhydrophobic copper surface is rare. Guo and co-workers prepared copper surface through reduction of copper sulfate by sodium borohydride.[45] But they have prepared superhydrophobic copper surface on sponge material only under magnetic stirring. Xi et al.[46] developed superhydrophobic copper surface on copper plate by electroplating from copper sulfate, while Pitchumani et al.[47] prepared through two-step electrodeposition process from the same substrate to fabricate copper on copper plate. But these methods have some draw-backs. For instance, they are not the direct fabrication of copper. Actually these methods elucidate that copper is fabricated on copper plate only, not on other substrates. Additionally, these methods are not convenient because the manipulation necessitates costly instrument and power supply. Furthermore, the fabrication by these methods could be done by applying certain range of voltages. Hence, these drawbacks inspired us to develop a facile, convenient, direct, economical, and universal method to prepare superhydrophobic copper surface on various substrates for useful applications. We developed the suprehy-drophobic copper surfaces for exquisite roll-off, self-cleaning, and oil/water separation ability by simple chemical reaction using cost-effective starting materials on various substrates such as glass, cotton, textile, silicon substrate, and transparency sheet under free-standing conditions. Appreciably, the procedure does not require any additional layer of low surface energy material. Moreover, the copper nanoparticle (CuNP) deposited on glass surface was found to exhibit antibacterial activity. The surface was formed through reduction of copper acetate by hydrazine to copper nanoparticles followed by natural deposition of the same on different surfaces of interest.

■ EXPERIMENTAL SECTION

Materials. All the reagents were of analytical reagent grade. Copper acetate monohydrate $[Cu(CH_3COO)_2 \cdot H_2O]$ and hydrazine hydrate

$(N_2H_4 \cdot H_2O; 80\%)$ were purchased from E-Merck. Glass apparatus were purchased from Blue Star, India, and they were properly cleaned with aqua regia and water and dried before use.

Analytical Instrument. Powder X-ray diffraction (XRD) was done in a PW1710 diffractometer, a Philips, Holland, instrument. The XRD data were analyzed by using (JCPDS) software. Field emission scanning electron microscopy (FESEM) was performed with a supra 40, Carl Zeiss Pvt. Ltd. instrument. The chemical state of the element on the surface of the nanomaterial was obtained X-ray photoelectron spectroscopy (XPS) measurements, carried out by a VG Scientific Escalab MK II spectrometer equipped with a Mg Kr excitation source (1253.6 eV) and a five-channeltron detection system. The average contact angle was evaluated at different positions of the same surface using a digital still camera (Sony Cyber-shot 8.2 megapixels). During this experiment there was no disturbance such as change in air flow or mechanical vibration. The rolling-off, self-cleaning, and water−kerosene separation experiments were performed, and images were reproduced using the same camera.

Synthesis of Copper Surface on Various Substrates. Fabrication of copper nanoparticles on various substrates such as glass, transparency sheet, silicon substrate, cotton wool, and textile was carried out through the chemical reduction of copper acetate by hydrazine hydrate at room temperature under closed condition or in open air. In a typical procedure, 0.25 mmol (50 mg) of copper acetate monohydrate was taken in a vial and dissolved in 4.8 mL of water. Next 200 μL of hydrazine hydrate (80%) was added dropwise. Then a glass slide of desired size (cut and cleaned) was placed into the vial at an angle of ~45−60° (as shown in the diagram [Figure S1] in Supporting Information). The whole reaction set up was kept for 12 h at room temperature in closed condition. Copper nanoparticles of fine resdish-brown color were deposited onto the surface of the glass slide as depicted in Supporting Information. The glass slide was removed from the vial carefully, washed gently with water and ethanol using a micropipette, and dried in vacuum. The drying was done for 3 to 5 d. Then the superhydrophobicity experiments and characterization were performed. The fabrication processes on transparency sheet, silicon substrate, cotton wool, and textile were done similarly. In cases of fabrication on cotton wool and textile, the simple immersed condition was adopted.

Determination of Thickness of Copper Surfaces on Glass. The superhydrophobic copper surfaces on glass were prepared from the reactions of copper acetate and hydrazine hydrates of varied concentrations at room temperature (25 °C). Then coating thickness measurement of the copper surfaces (of copper nanoparticles coated glass surfaces) was carried out using stylus-type surface profilometer (Dektak 150). The respective average step heights were recorded as the representation of thickness.

Determination of Water Contact Angle. Water droplets (5−20 μL) were dispensed carefully on the glass slide to determine the WCA. We performed the experiment at different positions of the same surface (i.e., on the same substrate), and the performances were recorded using a digital camera; average contact angles have been reported. During the experiment, air flow and mechanical vibration were completely avoided. The superhydrophobicity on other substrates such as glass, transparency sheet, silicon substrate, cotton wool, and textile was also executed carefully by dispensing water droplets, and digital images were obtained.

Roll-off Property of the Surfaces. We checked also the roll-off property of the as-prepared surfaces by means of moving a water droplet. First, the water droplet was dispensed on a surface. Then the droplet was run by the tip of the micropipette. Video of the experiment was recorded by the same digital camera.

Study on Self-Cleaning Property. The self-cleaning property of the as-prepared surfaces was tested by deposition of graphite powder on the as-prepared surface and subsequently cleaned by the directed movement of water droplets using the tip of a micropipette. The digital pictures were obtained at different moments in time.

Kerosene−Water Separation. Kerosene-water separation test was performed using as-prepared superhydrophobic cotton substrate. The two-necked glass apparatus having two outlets was placed below the

buret. The buret contains mixture of water and kerosene. One beaker was placed just below the upper outlet. The superhydrophobic cotton was embedded in the upper neck and below the upper outlet of the glass apparatus. The glass apparatus was securely placed vertically, and the buret was held by a clamp (discussed in detail with image under Results and Discussion section).
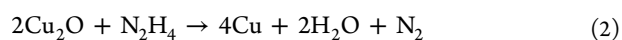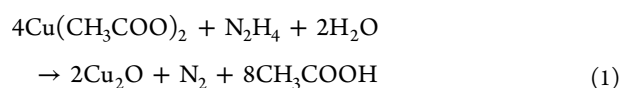
Water−kerosene mixture was poured slowly onto the as-prepared cotton. Water was removed through the upper outlet by the as-prepared superhydrophobic cotton wool and collected in beaker. On the other hand, kerosene passed through the cotton and was stored at the bottom of the glass apparatus. The digital images and videos were recorded at different moments in time.

Antibacterial Activity Assay. Antibacterial activity of copper nanoparticles (scooped using a spatula from the as-prepared Cu-coated glass surface) was tested against Gram-positive *Staphylococcus epidermidis* (NCIM 2493) and Gram-negative bacteria like *Escherichia coli* (MTCC N0. 443) and *Enterobacter cloacae* (MTCC N0. 509). The preliminary antimicrobial susceptibility was tested according to Kirby−Bauer disk diffusion method.[48] Briefly, an aliquot of bacterial stock was grown overnight at 37 °C in nutrient broth and standardized to 0.5 McFarland standards (10^6 cfu ml^{-1}). The standardized cell suspensions (100 μL) were spread on a Mueller−Hinton agar (Hi Media), and presoaked CuNP filter disks (5 mm diameter) were placed on the agar surface. Inhibition zone was measured after 24 h of incubation at 37 °C. The minimum inhibitory concentration (MIC) was determined by following the broth microdilution method according to Clinical and Laboratory Standards Institute (CLSI)[49] guidelines. A range of CuNP concentrations (0.005 to 5 mg mL^{-1}) was added to sterile 96-well microtiter plates, and the volume was brought to 300 μL well^{-1} with Mueller−Hinton broth. Culture of the strain was added to the mixtures in such a way that the total inoculum load was 10^5 cells well^{-1}. Finally, microtiter plates were incubated at 37 °C for 24 h. Bacterial growth was measured by the optical density at 600 nm using a Multiskan Spectrum spectrophotometer (model 1500; Thermo Scientific, Nyon, Switzerland). The MIC value of the CuNPs was determined by comparing the cell densities with wells where no CuNPs was added as positive control, and no bacteria with different test concentrations (uninoculated control) were used as negative control to maintain the sterility as well as blank.

RESULTS AND DISCUSSION

Synthesis of Copper Surface on Various Substrates. Fabrication of copper surface on various substrates such as glass, transparency sheet (plastic), silicon substrate, textile, and cotton wool was accomplished through the synthesis of CuNP from copper acetate followed by its automatic immediate deposition on the surface of the desired substrate as per the diagram given in Figure S1 of Supporting Information. Copper nanoparticle generation from copper acetate monohydrate through the reduction by hydrazine hydrate occurred according to eqs 1 and 2. We selected N_2H_4 because of its strong reducing capability and ligating power at higher hydrazine concentration. Then hydrazine can easily reduce Cu_2O to Cu(0). Initially cuprous oxide was formed by reduction of copper acetate by hydrazine hydrate. Since the hydrazine hydrate is a strong reducing agent it reduced cuprous oxide further to generate copper nanoparticles. Then CuNPs got deposited automatically on the surface of the substrate.

$$4Cu(CH_3COO)_2 + N_2H_4 + 2H_2O$$
$$\rightarrow 2Cu_2O + N_2 + 8CH_3COOH \tag{1}$$

$$2Cu_2O + N_2H_4 \rightarrow 4Cu + 2H_2O + N_2 \tag{2}$$

The process was carried out using 0.25 mmol of copper acetate monohydrate (in 5 mL of aqueous solution) at room temperature for suitable fabrication to show superhydrophobicity on all types of substrates as mentioned earlier. It could also be conducted using low scale (0.1 mmol) to large scale (1 mmol). However, pleasantly superhydrophobic copper surfaces of different thicknesses were also fabricated on glass surfaces using different concentrations of reactants. We found that the thickness of the CuNP coating was realized by tuning the concentration of copper acetate and hydrazine hydrate. The superhydrophobic copper surfaces of thickness 1.1, 2.9, 20.6, and 22.7 μm were deposited from the reactions of copper acetate of 0.125, 0.25, 0.50, and 0.75 mmol with 100, 200, 400, and 600 μL hydrazine hydrates, respectively, at room temperature (25 °C). We performed the coating thickness measurement of all these copper surfaces of copper coated glass surfaces using profilometer. The graphical representations of thickness (average step heights) are shown in Figure S2 of Supporting Information (see Table S1of Supporting Information also).

In this context it is imperative to mention that the ratio of $Cu(OAc)_2$ to hydrazine was observed to be crucial. We found that reaction between $Cu(OAc)_2$ and lower concentration of N_2H_4 leads to Cu_2O [0.25 mmol of $Cu(OAc)_2$ + 20−30 μL of N_2H_4 in 5 mL of H_2O] (see Figure S3a in Supporting Information for XRD) or Cu(0) + Cu_2O [0.25 mmol of $Cu(OAc)_2$ + 40−80 μL of N_2H_4 in 5 mL of H_2O] formation. The reaction between $Cu(OAc)_2$ and N_2H_4 leads exclusively to Cu(0) at higher hydrazine concentration [0.25 mmol of $Cu(OAc)_2$ + 200 μL of N_2H_4 in 5 mL of H_2O]. Hence we use 200 μL of N_2H_4 to extinct the possibility of formation of Cu_2O.

This is a thermodynamically driven reaction. Textbook information goes as follows at room temperature:

$$Cu^{2+}/Cu^+, E_0 = 0.158V \tag{3}$$

$$Cu^+/Cu, E_0 = 0.522V \tag{4}$$

$$Cu^{2+}/Cu, E_0 = 0.340V \tag{5}$$

$$N_2H_4/N_2, E_0 \text{ at higher pH} = -1.16V \tag{6}$$

$$N_2H_4/N_2, E_0 \text{ at lower pH} = -0.23V \tag{7}$$

From this it is understood that, with increase of pH, reduction potential of hydrazine decreases, but still it is lower than that of Cu^{2+}/Cu^+, Cu^+/Cu, and Cu^{2+}/Cu couple. So, anyway N_2H_4 can reduce Cu^+ to Cu even if in lower pH also.

So, the increased reductant concentration alters the formal potential, and the excess hydrazine drives the reaction to Cu(0) stage for completion. This is authenticated by ex situ XRD studies. The intermediate oxidation state of copper (Cu_2O) even at higher hydrazine concentration (0.25 mmol of $Cu(OAc)_2$ + 200 μL of N_2H_4) has now been authenticated by ex situ XRD studies during the reaction (after the elapse of 5 min). It may be elucidated that surface supports like glass, textile, etc. may also play a role for the reduction from the defect pattern of the material surface in addition to thermodynamic consideration.

There are many fabulous advantages of this developed method. The whole process does not require any stirring. The process was executed within 12 h under closed condition at room temperature. In the open atmosphere, the surfaces were also achieved that render similar superhydrophobicity character. It is imperative to mention that during the fabrication process on the flat and hard substrates such as glass slide, transparency sheet (a common plastic, typical polymer of cellulose acetate), and silicon substrate, the same could easily be immersed in an incline position (angle of ∼45−60°) to show better superhydrophobicity

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than by the surface prepared with lower or higher angle. On the other hand, the fabrication of irregular and soft surfaces such as textile and cotton wool was adopted by the simple immersion of the substrates. Other significant characters of this developed method are that the CuNP synthesis was achieved without using any capping agent or coreagent, the immerged undisturbed reaction condition offers deposition of copper nanoparticles on surfaces of different substrates, etc. Significantly, the method does not necessitate any application of additional layer of low surface energy material. Overall the fabrication process is facile, convenient, cost-effective, and one-pot free-standing method. Interestingly, the as-prepared superhydrophobic CuNP-coated glass surfaces were found to withstand water, base, acid, and thiol action and remain unaffected at room temperature. We tested the durability of superhydrophobic copper-coated glass surfaces by immerging under water (10 min), mild alkali (5 min in saturated aqueous $NaHCO_3$ of pH $\approx$ 9), acids (10 s in dilute HNO_3, H_2SO_4 of pH $\approx$ 5), and thiol (10 s in neat 1-octanethiol) at room temperature. After immersion the copper-coated glass surfaces were washed subsequently with water and ethanol and then were dried and tested for superhydrophobicity. We observed that these water, base, acids, and thiol-treated copper coated glass surfaces retain the original superhydrophobic character. Thus, air pocket on copper surface keeps aside H_2O, $NaHCO_3$, HNO_3, H_2SO_4, and 1-octanethiol, which demonstrates uniqueness of the film. Another significant feature of this CuNP fabrication method is the adhesion of CuNPs onto the surface. In most cases, surface functionality out of the five surfaces (we used for the fabrication of CuNPs) is −OH group, which invites Cu(II) ions from the precursor copper(II) acetate solution for bonding. The deposition of Cu(0) takes place on the respective surfaces after hydrazine reduction depending upon the surface morphology (roughness) and porosity. Among all the surfaces, the plastic surface easily removes the as-deposited metallic copper out of feeble mechanical abrasion. Other surfaces withstand wear and tear especially the textile and cotton surfaces because of their inherited uneven surface structure. Because of the above-mentioned advantages of copper surfaces, it is anticipated that this fabrication method would find application in surface science and material chemistry.

Characterization of the As-Prepared Surface. The as-prepared surfaces were characterized by XRD analysis. Figure 1
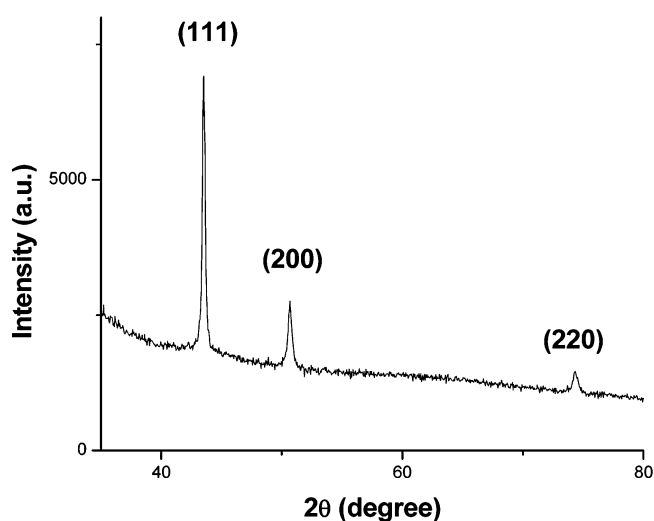

Figure 1. XRD pattern of copper nanoparticles on as-prepared glass surface.

shows the XRD pattern of the CuNPs of the as-prepared glass surface and agreed well with the reported data [JCPDS Card No. 04−0836]. The pattern illustrates three characteristic peaks at 43.5°, 50.6°, and 74.3° for the indices (111), (200), and (220), respectively. We also performed the XRD analysis for the copper nanomaterial deposited on the other substrates (i.e., silicon substrate, transparency sheet, cotton wool, and textile). All the XRD patterns displayed similar characteristic peaks (Figure S3b−e in Supporting Information). These patterns also indicate that the as-prepared surfaces are comprised of pure copper material devoid of any impurity or its oxide.

To determine the purity of the as-prepared surface we performed also XPS analysis. Figure 2 shows the peak locations
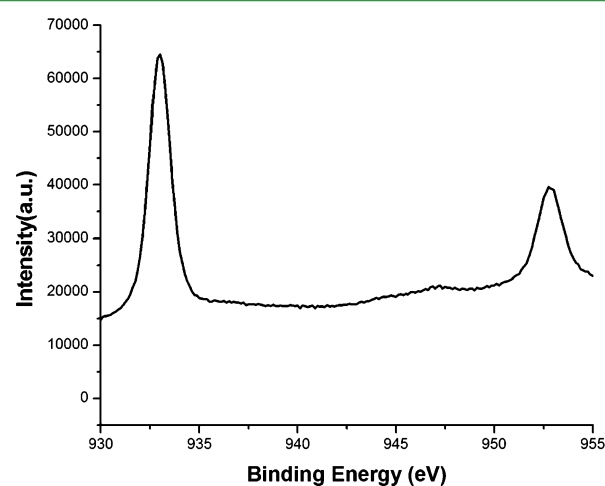

Figure 2. XPS pattern of copper (0) nanoparticles on as-prepared glass surface.

of the copper element. The peaks at 932.9 eV (Cu 2p3/2) and 952.8 eV (Cu 2p1/2) are assigned in Cu 2p region of copper and illustrate the lack of impurity of the as-prepared sample. However, there might be surface oxidation of copper of the as-prepared surface on keeping it for long time.

The morphology of the as-prepared surfaces was analyzed by the FESEM. Figure 3 shows the FESEM images (Figure 3a,b) of the superhydrophobic copper surface on glass. The high mangnification image displays that the CuNPs are of spherical polygonal nanosphere structure with diameter of a few hundred nanometers. The deposition of CuNPs is irregular, and overall the as-prepared surface is rough. However, there are also pores on the as-prepared surfaces. The FESEM of as-prepared surfaces on other substrates (silicon substrate, transparency sheet, cotton wool, and textile) were also studied, and their morphologies (Figure 3c−m) display the similar architecture as that of as-prepared glass surface. However, the surface morphology of the as-prepared surfaces varies widely. The rough surfaces (cotton wool and textile) become a bit smoother due to CuNPs deposition. On the other hand, smooth surfaces (glass, silicon substrate, and transparency sheet) roughen a little. It is worth mentioning that the defects on the substrate promote the facile growth of CuNPs. The nanocrystals are growing or initiated by the defects.[50]

However, the sizes of CuNPs deposited on various substrates are different. The sizes of CuNPs on glass, silicone substrate, and transparency sheet range between ∼500−800 nm (shown in
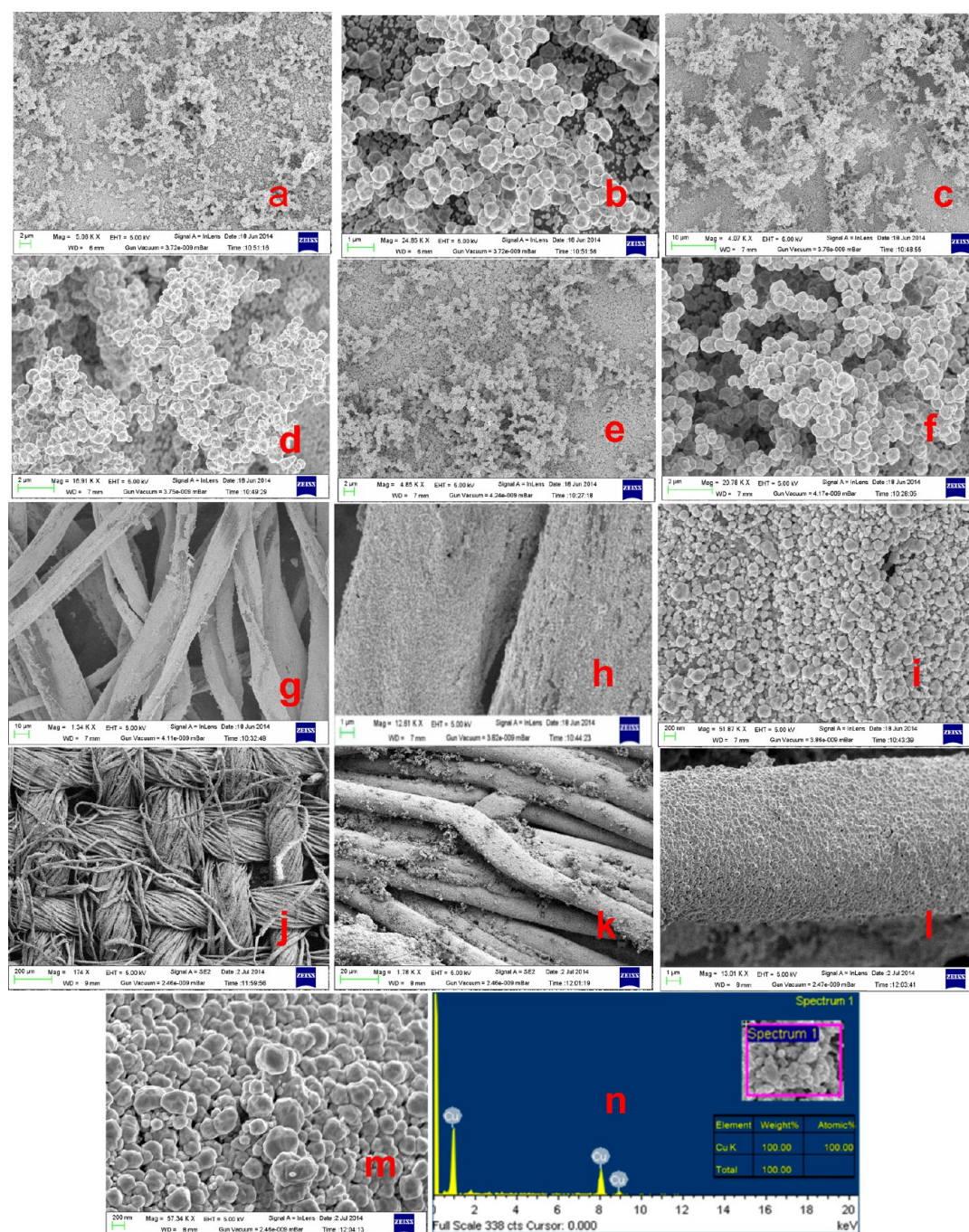
Figure 3. FESEM images at different magnification of as-synthesized glass (a, b), silicon substrate (c, d), transparency sheet (e, f), cotton wool (g–i), and textile (j–m) surfaces, and EDX of as-prepared glass (n) surface.

Table S2 in Supporting Information). On the other hand, the sizes of CuNPs deposited on textile and cotton wool range between ~200–800 nm and ~50–300 nm, respectively (Table S2 in Supporting Information).

The as-prepared surface was also tested by EDX analysis to identify the purity of the as-prepared material. Figure 3n shows the presence of 100 wt % of Cu in the EDX spectrum. This result indicates the purity of the as-prepared surface, which matched well with the XRD studies.

■ WETTABILITY PROPERTIES OF THE AS-PREPARED SURFACES

In this piece of work we prepared CuNPs deposited rough surfaces to achieve the wettability and adhesive properties such as superhydrophobicity, rolling-off, and self-cleaning properties of the as-prepared surfaces. Such properties have significant values in the field of surface chemistry. The superhydrophobicity character of the as-prepared surfaces was evaluated by measuring the WCA using a digital camera at room temperature. It is found from the contact angle measurements that all the as-prepared surfaces are superhydrophobic. Additionally, rolling-off and self-cleaning properties have also been tested through practical experiments. However, the superhydrophobicity as well as the oleophilicity of an as-prepared substrate also proved to be efficient for water–oil separation.

To evaluate the superhydrophobic character of the copper surface deposited on glass slide, we conducted the WCA measurements by
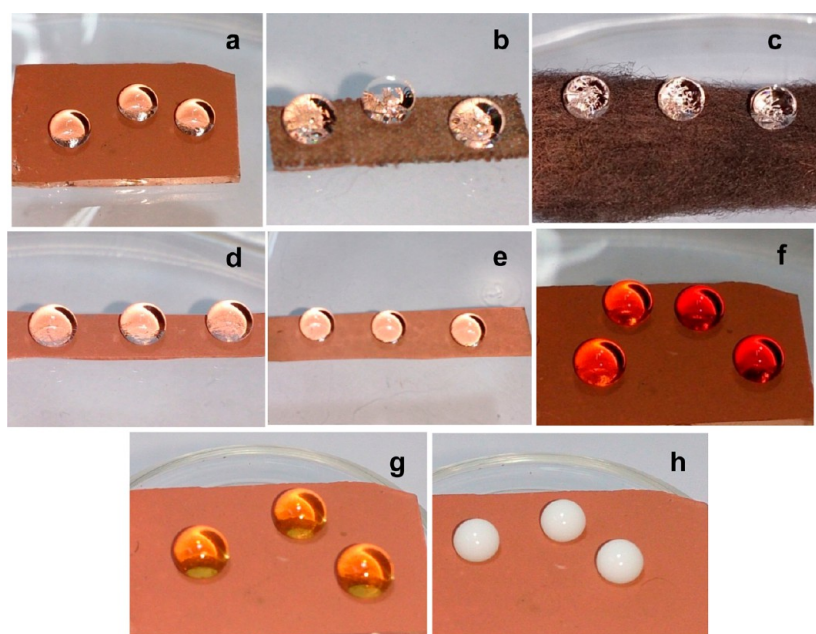
Figure 4. Normal deionized water droplets on as-prepared glass (a), textile (b), cotton wool (c), silicon substrate (d), and transparency sheet (e) surfaces; dye water on glass (f), tea on glass (g), and milk on glass (h) surfaces.

using 5−20 μL droplets. Figure 4a shows the spherical droplets of 20 μL on a glass slide. To find the relationship between WCA and volume of droplets, 5, 10, 15, and 20 μL droplets were dispensed on an as-prepared glass slide (Figure S4 in Supporting Information). We observed that a spherical water droplet of 5 μL displays a 164° WCA signifying the superhydrophobic character of the surface. However, the experiment illustrates inverse relationship between WCA and volume of water droplets. Upon increasing the volume of water droplets (5 to 20 μL), there is a sharp decrease in WCAs due to the mass effect of water droplets. We found that water droplets of 5, 10, 15, and 20 μL show the average contact angles of 163 ± 2°, 161 ± 2°, 158 ± 2°, and 155 ± 2°, respectively. We investigated also the change of superhydrophobic character with thickness of copper surface on glass (Table S1 in Supporting Information). It was observed that WCA is highest for the glass surfaces prepared from the reaction of 0.25 and 0.50 mmol copper acetate with 200 and 400 μL hydrazine hydrate, respectively, while the reaction was performed in 5 mL of water (see Table S1 in Supporting Information).

The developed methodology on the glass slide was explored to prepare the similar superhydrophobic surfaces on other solid and flat substrates such as silicon substrate and transparency sheet (plastic material) also. It is to be noted that researchers paid attention to develop superhydrophobic surfaces on rigid solid surfaces (such as silicon substrate, glass slide, metals etc.) because the wettability of such surfaces plays important roles in daily life, industry, and agriculture.[51,52] The preparation of superhydrophobic plastic material is also indispensible and challenging task.[53] Figure 4(d, e) shows the water droplets of 20 μL situated on silicon substrate and transparency sheet indicating the superhydrophobicity. We found also that the WCAs on glass, silicon substrate, and transparency sheet are less than 20° (Figure S5 in Supporting Information). The contrast wettability characteristic between normal glass/silicon substrates/transparency sheet (WCA < 20°) and CuNPs deposited glass/silicon substrates/transparency sheet substrates (WCA > 160°) confirms that as-synthesized CuNP deposited surfaces are highly superhydrophobic due to the CuNP deposition.

Fabrication of superhydrophobic cotton and textiles is an important area of research due to thei vital practical applications such as water-resistant apparel, plastron layer, etc.[52,54,55] We applied our methodology to create CuNPs deposited superhydrophobic textile and cotton wool, which could find different applications in cotton and textile engineering. Figure 4b,c presents the water droplets of 20 μL volume situated on as-prepared textile and cotton wool indicating their fabulous superhydrophobicity. However, we observed that superhydrophobicity of the as-prepared surfaces does not depend upon the size of CuNPs (shown in Table S2 in Supporting Information). It is found that the as-prepared glass, silicone substrate, and transparency sheet having CuNPs of diameter ∼500−800 nm render higher WCA than as-prepared textile (CuNPs of diameter ∼200−800 nm) and cotton wool (CuNPs of diameter ∼50−300 nm) surfaces (Table S2 in Supporting Information). Apart from these, we tested the superhydrophobicity of these surfaces toward dye water, tea, and milk also (shown in Figure 4f−h).

For the elucidation of the aforesaid superhydrophobic character of the as-prepared surfaces, two theories (the Wenzel and the Cassie−Baxter)[9,10] were considered. These models explain the effect of morphology and surface roughness on the apparent liquid contact angle. Depending on the surface roughness, the contact surface area between water droplet and surface could be continuous or discontinuous.[56] The former case (continuous) is the Wenzel model for deposition of liquid drop where the droplet impregnates on the surface. This phenomenon (Wenzel equation) could be designated as follows:

$$\cos \theta_w* = r_f \cos \theta y \qquad (8)$$

Here, θ_w* is the apparent WCA on the rough surface, θy is the Young contact angle of the liquid droplet on the smooth surface, and r_f is the Wenzel roughness or Wenzel factor of the surface defined as specific area (real area)/projected area (over horizontal plane). The equation demonstrates that hydrophilicity of hydrophilic surface and hydrophobicity of hydrophobic surface increases as r_f increases. This equation
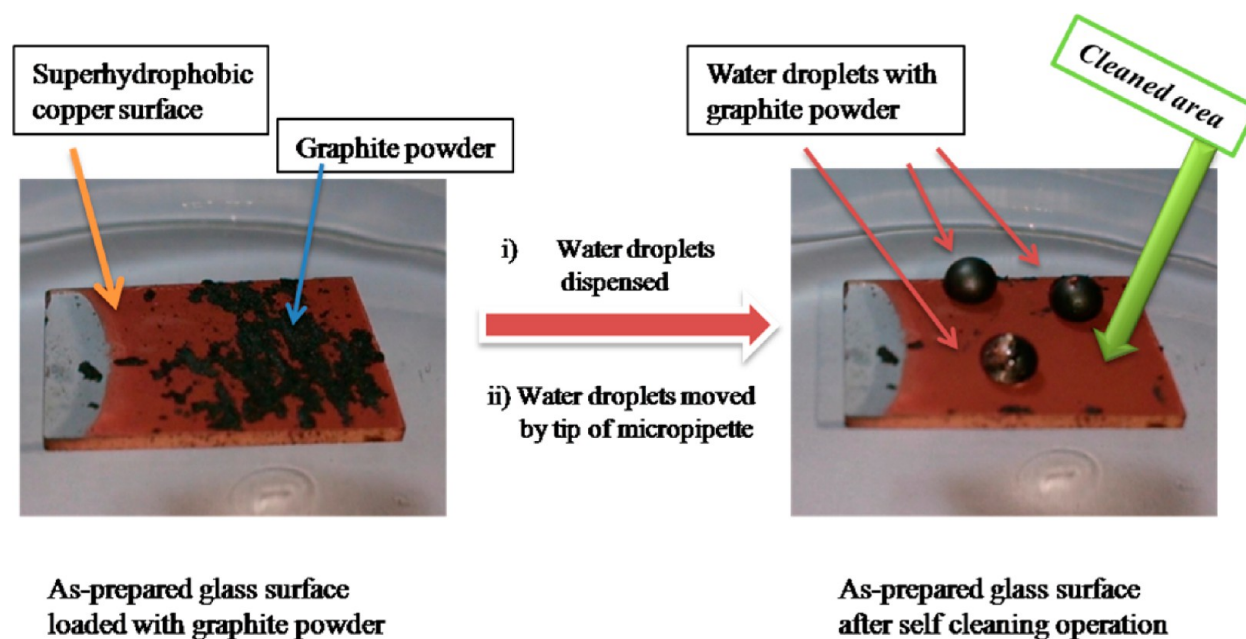
Figure 5. Self-cleaning property test: graphite powder loaded as-prepared glass surface is cleaned by moving water droplets.

mainly is applicable for the surface having low to moderate surface roughness where the liquid droplet infuses into the surface. This model also implies that a water droplet is sticky to surface due to significant adhesion between the droplet and the surface.

On the other hand, the discontinuous contact surface area between water droplet and surface could be explained by the Cassie–Baxter state, where a liquid droplet, dispensed on the surface, sits on the top of the asperities and traps the air pockets below the droplet. This state could be defined by eq 9 as follows:

$$\cos \theta cb* = \psi(1 + \cos \theta y) - 1 \qquad (9)$$

where $\theta cb*$ is the apparent WCA, ψ is the area fraction of solid that touches the liquid, and θy is the Young contact angle. This theory demonstrates that a liquid droplet sits on asperities generating air cavities giving rise to decrease in solid–liquid interface and increase in liquid–vapor interface. Consequently, the liquid droplet is nonsticky to the surface; that is, the adhesion between droplet and surface is low. This leads to the roll-off property of the droplet on the surface.

The morphological study of the as-prepared surfaces indicates that the surfaces have roughness and many cavities that trap air in between the water droplet and surface when water droplets are dispensed on the surfaces. So the dispensing of water droplets on the as-prepared surfaces is the Cassie–Baxter state, and droplets could not penetrate onto surface due to the presence of air pockets. Accordingly, the water droplets on the as-prepared superhydrophobic surfaces render high WCA and become nonsticky. Thus, water droplets would roll-off on the as-prepared surfaces.

Roll-off Property of the As-Prepared Surfaces. Because of the nonsticky behavior of water droplet on surface in Cassie–Baxter state, the water droplet rolls off easily on the surface. The as-prepared superhydrophobic surfaces render this property also. We investigated that a water droplet of 20 μL on glass could easily move directed by the tip of a micropipette (see Video File 1 in Supporting Information) on horizontal as-prepared glass surface. Moving on the surface, the water droplet does not adhere to the surface left. We found also that the similar consequence

emerged when a water droplet dispensed on the slightly tilted as-prepared glass surface.

Self-Cleaning Property of the As-Prepared Surfaces. Superhydrophobic surfaces with self-cleaning ability have become a leading research topic in surface science and technology due to their various potential and practical applications.[15,16,57,58]

In the following experiment we presented the self-cleaning property of our as-prepared hydrophobic glass surface. Water droplets were dispensed on the horizontal as-prepared glass surface heavily loaded with dust particles (in our case we used graphite powder). As the water droplets rolled-off guided by the tip of a micropipette, these removed graphite powder adequately (see Figure 5 and Video File 2). As a result, the dirty surface became a cleaned surface (shown in the picture by green arrow). Moreover, the investigation was carried out by dispensing water droplets on the tilted glass surface (nearly horizontal) adhered graphite powder, which resulted in a similar consequence. This self-cleaning character of superhydrophobic copper material could be applied to protect surface or material from corrosive reagents and microbes.

Kerosene–Water Separation by the As-Prepared Substrate. Because of the increasing industrial oil–mixed wastewater and frequent oil-spill accidents, oil–water separation is a big challenging task wordlwide.[59,60] Herein we disclosed a kerosene–water separation method using our as-prepared modified superhydrophobic cotton wool substrate. Before executing the oil–water separation experiment we tested that as-prepared CuNP deposited superhydrophobic cotton substrate is found to be superoleophilic (see Figure S6 in Supporting Information). From the experiment, it was observed that our as-prepared superhydrophobic cotton did not permeate the water droplet but adsorbed kerosene. Afterward, we performed the kerosene–water separation according to the experimental setup as per Figure 6. In the experimental setup for kerosene–water separation, we used a coilless straight condenser closed at one end having two arms. The glass apparatus was placed below the buret. The buret contained a mixture of water and kerosene. We embedded the superhydrophobic–superoleophilic cotton wool
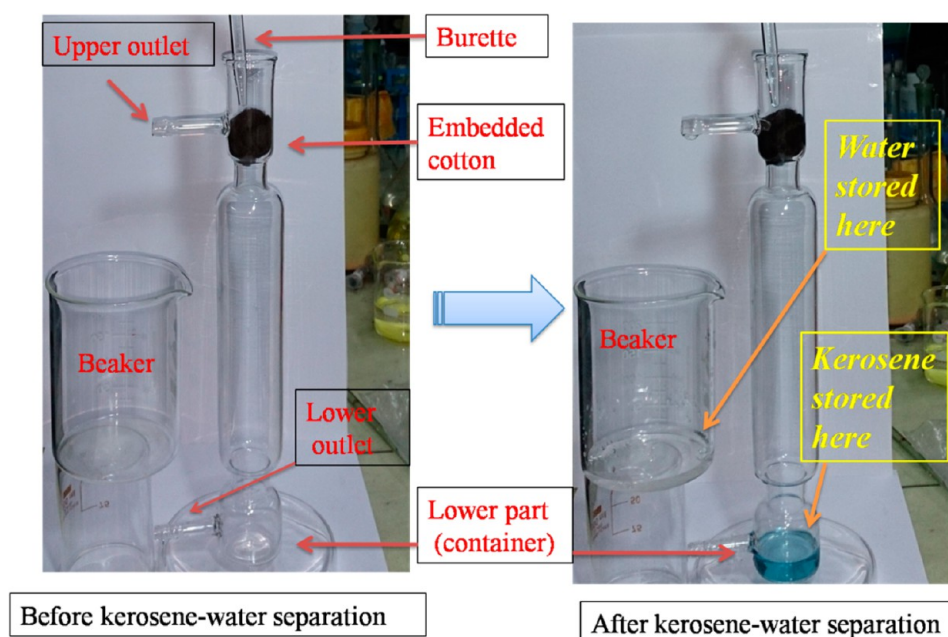
Figure 6. Kerosene−water separation by the as-prepared superhydrophobic cotton wool.
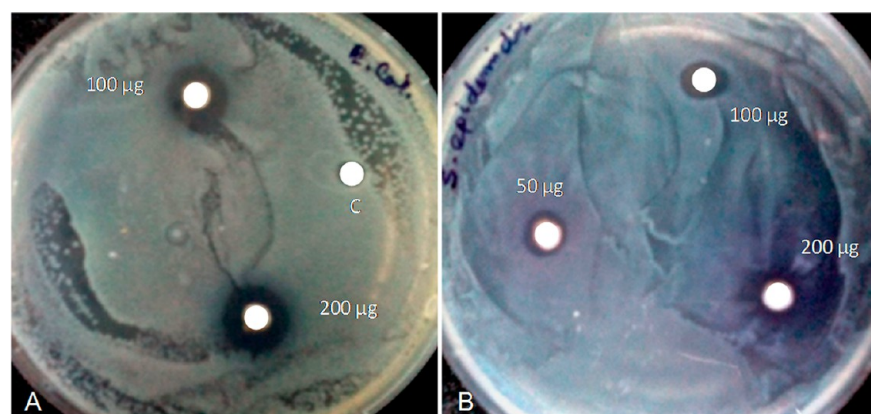

Figure 7. Inhibition zone of different concentration of CuNPs against *E. coli* (MTCC N0. 443) (A) and *S. epidermidis* (NCIM 2493) (B) on Mueller−Hinton agar medium.

in the upper neck and just below the upper outlet of the glass apparatus. Water−kerosene mixture was poured slowly onto the as-prepared cotton. Water was removed through the upper outlet by the cotton and was collected in beaker (see also Video File 3 of the Supporting Information). And kerosene passed through the cotton and stored at the bottom of the glass apparatus.

Antibacterial Activity Assay of As-Prepared Copper Nanoparticles. The antimicrobial activity of CuNPs was compared for different microorganisms using two established measures: inhibition zone (Figure 7) and minimum inhibitory concentration (Table 1). Preliminary screening of CuNPs against *E. coli*, *E. cloacae*, and *S. Epidermidis* showed its higher effectiveness toward Gram-negative bacteria (*E. coli* and *E. cloacae*) compared to Gram-positive *S. Epdermidis* (Figure 7). This phenomenon was further supported by minimum inhibitory concentration (MIC) values as shown in Table 1. The MIC values of CuNPs were found to be 78 μg mL^{-1} for both the Gram-negative bacteria (*E. coli* and *E. cloacae*) and 156 μg mL^{-1} for Gram-positive *S. epidermidis*. The result shows good agreement with previously reported literature.[61] The sensitivity of CuNPs was found lower in case of *S. Epidermidis* as the strain is

Table 1. Minimum Inhibitory Concentration (MIC) of Copper Nanoparticles for Various Microorganisms

name of the organism	MIC (μg mL^{-1})
Escherichia coli	78
Enterobacter cloacae	78
Staphylococcus epidermidis	156

well-known for its multidrug-resistance property.[62] The selected CuNPs are likely to be effective in killing a range of bacterial pathogens related to hospital-acquired infections as well as food- and water-born infections.

■ CONCLUSION

We have successfully prepared superhyrdophobic surfaces of copper nanoaparticles on various regular and irregular substrates such as glass, cotton wool, textile, silicon substrate, and transparency sheet through facile, cost-effective, and distinctive fabrication technique. The developed method was accomplished through simple chemical reduction of copper acetate by hydrazine on free-standing at room temperature. The as-prepared rough

porous surfaces displayed significant superhydrophobic, rolling-off, and self-cleaning properties. Water contact angle was found to be $164 \pm 2°$ for a 5 μL droplet. Superhydrophobic CuNP-coated glass surface distinctively withstands water (10 min), mild alkali (5 min in saturated aqueous $NaHCO_3$ of pH $\approx$ 9), acids (10 s in dilute HNO_3, H_2SO_4 of pH $\approx$ 5) and thiol (10 s in neat 1-octanethiol) at room temperature (25−35 °C). The as-prepared cotton wool has been applied for effective water−kerosene separation due to its superhydrophobicity and oleophilicity, whereas superhydrophobic CuNP (deposited on glass surface) exhibits antibacterial activity against both Gram-negative and Gram-positive bacteria. Because of having momentous wettability properties of the as-prepared surfaces, it is anticipated that this flourishing developed technology would find many industrial and biological applications.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthetic diagram, XRD analysis, digital images of WCA and WCA versus volume of water droplet curve, and video files of roll-off, self-cleaning, kerosene/water separation. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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