Superhydrophobic carbon-based materials: a review of synthesis, structure, and applications

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Abstract

Materials with appropriate surface roughness and low surface energy can form superhydrophobic surfaces, displaying water contact angles greater than 150°. Superhydrophobic carbon-based materials are particularly interesting due to their exceptional physicochemical properties. This review discusses the various techniques used to produce superhydrophobic carbon-based materials such as carbon fibers, carbon nanotubes, graphene, amorphous carbons, etc. Recent advances in emerging fields such as energy, environmental remediation, and thermal management in relation to these materials are also discussed.

Key words: superhydrophobicity, carbon-based materials, surface energy, surface roughness

1. Introduction

Wettability of a solid surface describes the ability of a liquid to maintain contact with the surface, which is important in the bonding or adherence of two materials [1]. Dependent on both roughness and chemical heterogeneity, wettability is a very important characteristic in nature as well as in our daily life. Hydrophobicity and hydrophilicity are two principal wettability conditions. The surfaces of materials are hydrophilic if the water contact angle (WCA, θ) is in the range of 0° ≤ θ < 90° and they are hydrophobic if the WCA is 90° < θ ≤ 180°. Hydrophobicity is observed in nonpolar substances, which tend to aggregate in aqueous solutions and exclude water molecules.

Superhydrophobic materials have recently attracted attention from both academic and industrial circles because of their importance in fundamental research and potential industrial applications such as bio-surfaces, anti-biofouling, transparent and antireflective superhydrophobic coatings, structural color, fluidic drag reduction, enhancing water supporting force, prevention of water corrosion and oil-water separation, protective coatings, preventing adhesion of water and snow to windows or antennas, self-cleaning, enhancing buoyancy, and coating films for electronic devices [2-8].

The phenomenon of superhydrophobicity was first studied by Johnson and Dettre [7] in 1964 using rough hydrophobic surfaces. They developed a theoretical model based on experiments with glass beads coated with paraffin and polytetrafluoroethylene telomere, respectively. Barthlott and Ehler [9] studied the self-cleaning property of superhydrophobic micro-nanostructured surfaces in 1977, and they described such self-cleaning and superhydrophobic properties for the first time as the “lotus effect”. The superhydrophobic state of a surface is defined by the contact angle between a water droplet and the surface of a material that has a WCA above 150°. Superhydrophobic surfaces display a self-cleaning effect (water repellent) widely known as the “lotus effect.” Superhydrophobicity can be achieved either by selecting low surface energy materials or by introducing roughness [9-14].
Activated carbons, graphite, carbon fibers (CFs), fullerenes, carbon nanofibers (CNFs) (carbon nanotubes [CNTs], graphite nanofibers [GNFs]), micro-/meso-porous carbon, and, more recently, graphene carbon-based materials have emerged as extremely promising materials for various types of applications owing to their outstanding electronic and optical properties [15-28]. Recently, carbon-based superhydrophobic surfaces have been fabricated because of their promising applications such as conductive-transparent films, oil-water separation, and electromagnetic-interference-shielding [29-49]. In general, small water droplets on CF fabrics will be up to 120°, but not much greater for a flat surface.

To enhance the hydrophobicity of carbon-based materials, two approaches have been established recently [30-33]. First, research on superhydrophobic carbon-based materials has focused on increasing surface roughness by introducing geometric surface area.

Dip-coatings methods are also often employed to obtain superhydrophobic surfaces. As demonstrated by Nguyen et al. [31], iterative dip coating of a foam in a graphene solution allows desired amounts of graphene sheets to be deposited on the pore-wall surface of melamine foams, rendering the foams superhydrophobic and superoleophilic, with a WCA of 162° and a chloroform absorption capacity of 165 times their own weight (1.86 ton m⁻³) [31,50-52]. Second, various functional groups or additional organic/inorganic materials can be introduced to remarkably vary surface wettability [53-55]. For example, Zeng et al. [32] and Charinpanitkul et al. [52] reported a simple method to produce CNT-based films with exceptional superhydrophobicity and impact icephobicity based on deposition of acetone-treated single-walled CNTs (SWCNTs) onto glass substrates. The acetone-functionalized films showed a strong ability to mitigate ice accretion from supercooled water droplets (-8°C), and the droplets were found to bounce off the films tilted at 30°. The untreated nanotubes films did not display similar behavior, and the supercooled water droplets remained attached to the films’ surfaces. Such studies could serve as the foundation of highly versatile technologies for both water and ice mitigation.

Most current research on carbon-based materials has focused on their electrical, physiochemical, and mechanical properties [56-58]. In particular, surface properties such as robustness against environmental contamination are critical design considerations if intrinsic properties are to be maintained. Herein, we start by discussing the properties of carbon-based materials with superhydrophobic surfaces provided by emerging methods to create superhydrophobic surfaces with enhanced bulk properties. The recent advances in this field are summarized, including the wetting behavior of water on carbon materials such as CFs, CNTs, graphene, and amorphous carbons, and the formation of hierarchical structures and low surface energy chemical composition, with emphasis on fundamental understanding of related processes. Potential applications in energy, environmental remediation, and thermal management are also discussed [59-63].

In this paper, we discuss the recent theoretical advances in superhydrophobicity, the relation of superhydrophobicity to the more general type of “superpohic” surfaces, manufacturing methods to obtain superhydrophobicity with different kinds of carbon surfaces, and new potential applications of superhydrophobic carbon-based materials such as new energy technology, green engineering, underwater applications such as antifouling, and optical applications.

2. Theoretical Background

2.1. Surface roughness

Superhydrophobicity, as shown by lotus leaves, is an area that has received much interest in the past few years in relation to self-cleaning surfaces and other processes as well as in the design and production of artificial biomimetic surfaces [64-71]. Fig. 1 shows a structural diagram of the lotus effect [64]. The structures of a lotus leaf, i.e., branch-like nanostructures on top of micropapillae, have been carefully observed by scientists. These microscale-structures can induce superhydrophobic surfaces with large contact angles and low sliding angles. It is believed that this unique self-cleaning property is based on the surface lotus effect illustrated in Fig. 1. The roughness is caused by the microscale papillae and nanoscale tomenta (Figs. 1b-d). To construct superhydrophobic carbon-based material surfaces, it is essential to understand the wetting behavior of water on the surface of the carbons.

Superhydrophobic surfaces are generally expressed by the contact angle between a water droplet and the solid surface. Wenzel’s early works and later Cassie-Baxter’s work defined the importance of surface roughness and heterogeneity, which are now recognized as key parameters in the wettability of hydrophobic surfaces [65,66]. Wang et al. [71] and Yu et al. [72] showed that superhydrophobic lotus leaves have a peculiar wax with two scales of roughness (a: papillose epidermal cells around 10 μm; b: tubular wax crystals around 10 nm on the papillose epidermal cells).

Contact angle measurements, as described by Young in 1805,
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Fig. 2. Liquid droplet spreading on (a) flat surface (b) and rough surface (b-d). Depending on the roughness of the surface, the droplet is either in the so-called (a) Young’s state, (b) Wenzel’s state, (c) Cassie-Baxter’s state, and (d) an example of re-entrant morphology (color figure available online).

remain the most accurate method for determining the interaction energy between a liquid and solid in a condensed state at the minimum equilibrium distance of solid and liquid. When a droplet of water rests on a surface, the contact angle can be measured at the edge of the droplet (Fig. 1). Fig. 2 shows the liquid droplet wetting behavior of the corresponding theory: (a) Young’s state, (b) Wenzel’s state, (c) Cassie-Baxter’s state, and (d) an example of re-entrant morphology [5,11,14]. More than 200 years ago, Young, identified in a recent biography as “the last man who knew everything” [73], described the forces acting on a liquid droplet spreading on a flat surface (Fig. 1a).

On flat surfaces, Young’s equation defines the contact angle (θ) depending on the solid-vapor, solid-liquid, and liquid-vapor surface tensions, as given in Eq. (1), where γSV is the interfacial tension between solid and vapor, γSL is the interfacial tension between solid and liquid, and γLV relates to the interfacial tension between liquid and vapor. Depending on the value of θ as measured by water, if θ is less than 90°, the surface is conventionally described as hydrophilic; if θ varies between 90° and 150°, the surface is hydrophobic; and if θ is greater than 150°, the surface is conventionally described as superhydrophobic [74-81].

\[
\cos \theta = \frac{\gamma_{LV} - \gamma_{SL}}{\gamma_{SV}}
\]  
(1)

Depending on the level of surface roughness, two different models can be distinguished. The first, shown in Fig. 2b, is Wenzel’s state. The droplet maintains contact with the surface and fills the asperities, and the surface area associated with the contact angle is increased by the roughness factor r.

\[
r = \text{roughness factor} = \text{actual surface area} / \text{planar area}
\]  
(2)

Wenzel’s state is described by Eq. (3).

\[
\cos \theta_w = r \cos \theta = r \left(\frac{\gamma_{LV} - \gamma_{SL}}{\gamma_{LV}}\right)
\]  
(3)

In Eq. (3), r is equal to the ratio between the actual surface area of the rough surface and the projected (apparent) area, where the non-dimensional surface roughness factor \( r > 1 \). r emphasizes the effect of the surface chemistry determined by the term \( \cos \theta \), the non-dimensional surface roughness. When θ is less than 90°, an increase in the roughness factor r reduces \( \theta_w \), but if θ is higher than 90°, an increase in roughness leads to an increase in \( \theta_w \).

If the droplet is suspended on the surface asperities and the liquid does not penetrate the protrusions of the surface features, then this case belongs to Cassie-Baxter’s model. In this model, the apparent contact angle is the result of all contributions of different phases [82]. In Eq. (4), \( f_1 \) and \( f_2 \) are the fraction of the projecting solid and vapor on the surface, respectively, and \( f_1 + f_2 = 1 \). Eq. (4) only applies to cases where the liquid only contacts the top of the surface. However, a more complex version of Eq. (4) is required when partial penetration of the grooves occurs because the pores are filled with air. The hydrophobicity is enhanced by the increases of the vapor fraction. Because the pores are filled with air, which is hydrophobic, the contact angle always increases, relative to the behavior seen on a flat substrate having an identical chemical composition [82].

\[
\cos \theta_{CX} = r f_1 \cos \theta - f_2
\]  
(4)

From these two theories, it can be found that surface topography can enhance surface wettability on solid surfaces, whether they are hydrophobic or hydrophilic. This finding guides us to tune the surface wettability by controlling surface geometrical structures independently of the chemical composition [82-87]. On the other hand, the surface morphology was found to be an important parameter and more precisely “reentrant” structures are required to obtain such a superhydrophobic surface (Fig. 2d). These morphologies induce a negative Laplace pressure difference because they introduce a transition in the liquid-vapor interface from concave to convex, inducing a higher energy barrier between Wenzel’s states and Cassie-Baxter’s states [86,87].

2.2. Modification of roughness of low surface energy materials

Based on the general contact angle theory of Wenzel, two main approaches have been developed to generate superhydrophobic surfaces. One is increasing the surface area on a microscopic scale of low surface energy materials, as described above in Section 2.1; the other is to fabricate a suitable surface roughness with certain materials and subsequently modify the as-prepared surface with low surface energy materials [88]. The latter method is no longer limited to low surface energy materials, and it can be extended to the fabrication of hydrophobic surfaces for many systems. Various low surface energy materials have been developed to modify microscopic scale surfaces to form superhydrophobic surfaces. Fluorinated compounds, silane, and long alkyl chain fatty acids are typical low surface energy compounds, and have the ability to endow various substrates (SiO₂, TiO₂, Al₂O₃, metals, polymers etc.) with high hydrophobicity. Fig. 3 shows various surface reactive molecules for low-surface-energy modifications [88-90].

The surface energy is generally defined as the work required
In addition, the total surface energy of solids and liquids depends on the different types of molecular interactions, such as the London dispersive and the polar or acid/base interactions, and is considered to be the sum of these independent components [92].

In the early 1960s, Fowkes [93,94] introduced the concept of the surface free energy of a solid. The total surface free energy can be divided into the London dispersive and specific (or polar) components [93-95].

\[
g_s = g^L_s + g^P_s
\]  

(5)

where \(g_s\) is the total surface free energy, the subscript \(S\) represents a solid state, and \(g^L_s\) and \(g^P_s\) are the London dispersive and specific (Debye, Keesom of van der Waals, H-bonding, π-bonding, and other small polar effects) components of the surface free energy of the constitutive elements. The London dispersive and specific components are determined by measuring the contact angles of two testing liquids with known London dispersive and specific components. The surface free energy of a solid can be determined on the basis of contact angle measurements using the geometric mean, according to Fowkes’ proposition based on a solid (subscript \(S\))–liquid (L) droplet–air system, as described by the following equation [93]:

\[
g_s(1 + \cos \theta) = 2\sqrt{\gamma_s^L \gamma_s^P} + 2\sqrt{\gamma_s^P \gamma_s^P}
\]  

(6)

where \(\theta\) is the contact angle of a liquid droplet in the solid state.

As reported in our previous work, the specific component \(g^P_s\) is highly dependent on the surface functional groups, and the dispersive component \(g^L_s\) is largely dependent on the total electron density in the carbon [94].

3. Superhydrophobicity on CFs

CFs have attracted considerable interest due to their electrical properties, thermal conductivity, and high strength, lending outstanding behavior in practical applications [96-101]. In many cases, the CF surface properties are a crucial factor in their performance. Their specific surface area, however, is not sufficiently large for them to serve as ideal electrochemical materials compared to other carbon nanomaterials. Superhydrophobicity is an effect where roughness and hydrophobicity combine to generate unusually hydrophobic surfaces [81,100-105]. Because CFs are intrinsically hydrophobic, surface treatment is usually required to induce a hydrophilic state prior to their practical use [106-108]. The pristine hydrophobicity of CFs hinders their widespread utilization, and research on potential applications of this material generally has been limited.

Bliznakov et al. [100] used a simple and inexpensive route for the fabrication of a superhydrophobic metal surface. First, carbon/carbon composite paper (Toray TGP-H) is electroplated with copper. The copper layer is rendered hydrophobic by self-assembling a monolayer of dodecanethiol. The surface topography required to induce superhydrophobic behavior is achieved by varying the plating bath composition (Cl-, polyethylene glycol, and bis (3-sulfo)propyl disulfide additives) and the time of deposition (this varies the effective thickness of the Cu layer). The surface morphology created by the original arrangement of
the CFs in the Toray paper (diameter 8 μm, spacing 30 μm) does not produce superhydrophobic behavior. This is true for both continuous and incomplete copper coatings. Actual superhydrophobic behavior (large contact angles, 160-165°, and very small contact angle hysteresis, 2 to 3°) is achieved when a continuous copper layer is deposited on the CFs and secondary micrometer-range roughness is developed as a result of the formation of small copper crystallites (size ~1 μm).

Previous studies have mostly focused on post-treatment of the CF surface to render a chemical composition that promotes surface hydrophobicity. The Hsieh group has carried out research on developing superhydrophobic CFs. They demonstrated the influence of the fluorine/carbon (F/C) ratio on superhydrophobicity of CNFs prepared by a template-assisted synthesis (Fig. 4a) [109]. To functionalize the CNFs, the thermal chemical vapor deposition (CVD) method was used to deposit a fluorocarbon (using perfluorohexane as the precursor) coating on the surface of the CNFs at 100, 300, and 500°C. The resulting CNFs exhibited good water-repellent behavior owing to hydrophobic surface groups including -CF$_2$ and -CF$_3$ groups. The fluorocarbon coating improves the superhydrophobicity of the CNF array and an upward increase of contact angle of water with F/C ratio was observed, i.e., from 110° to 161°. The superhydrophobic behavior in this study can be explained by 1) the lower surface energies of fluorocarbon coated surfaces and 2) the highly rough CNF arrays. They also investigated a continuous forest of CNTs grown catalytically on microscaled polycrystalline (PAN)-based CF through a catalytic chemical vapor deposition (CCVD) technique, using Ni nanoparticles and acetylene as a catalyst and a carbon source, respectively (Fig. 4b) [40]. The nanotubes were successfully branched and decorated onto the CFs at different axes, forming a micro/nano carbon structure. The superhydrophobic surfaces are based on regularly ordered CFs (8-10 μm in diameter) decorated by CNTs with an average size of 20-40 nm. The contact angle of water significantly increases from 148.2 ± 2.1° to 169.7 ± 2.2° through the introduction of CNTs. This finding sheds light on how the two-tier roughness surface induces superhydrophobicity, and how the presence of CNTs reduces the area fraction of a water droplet in contact with a carbon surface with two-tier roughness. They also used a hydrophobic coating of silica nanoparticles onto microscaled CFs and investigated the superhydrophobic behavior of composite nano/microstructures (Fig. 4c) [41]. The two-tier composite surfaces are based on regularly ordered CFs (8-10 μm in diameter) that are coated with SiO$_2$ nanoparticles with an average size of 300-500 nm. The microscale fiber is used here to provide primary surface roughness, while the silica nanoparticles lend secondary roughness, mimicking the lotus leaf in nature. Increasing the density of silica on CFs had significant effects on the enhancement of the static contact angle, decrease of the contact angle hysteresis, and superhydrophobic stability. Without any subsequent low-surface-energy treatment, the unique composites with two-tier roughness exhibited superhydrophobicity with a high contact angle of 162.5 ± 2.2° with water. The results can be attributed to the higher density of silica coating resulting in more tortuous three-phase contact lines, thus facilitating the self-cleaning effect.

The aforementioned method for the growth of CNTs on CF surfaces has some drawbacks. For example, at the high synthesis temperature, the metal catalysts easily aggregate into large particles and form different kinds of carbon nanomaterials. In addition, these processes require purity to attain adequate superhydrophobic and electrochemical properties [104]. Park et al. [102] reported that high-density carbon nanomaterials can be prepared by the decomposition of C$_2$H$_6$ on CF surfaces coated with Ni-doped mesoporous TiO$_2$ film at lower temperature. Scanning electron microscopy (SEM) images indicated that GNFs with an average diameter of 40 nm grew uniformly and densely on CF surfaces (Figs. 5a-d). The contact angle of the CF surfaces increased from 27.2 to 153.5° after growth of GNFs and coating of a fluoropolymer (FP) (Figs. 5e-h). Deionized water, diiodomethane, ethylene glycol, and glycerol were selected for measurement of the contact angle of CFs. Table 1 shows the dispersive ($\gamma_d$), polar ($\gamma_p$), and surface free energy ($\gamma_s$) components of wetting liquids used in Park’s work: pristine CFs, oxidized CF-H, Ni-doped mesoporous TiO$_2$ film coated CFs, FP coated CFs, GNF coated CFs, and FP coated CF-GNFs. It is shown that the surface treatments significantly affect the surface energy of the CFs. The total surface free energy, $\gamma_s = \gamma_d + \gamma_p$, for CFs before the chemical treatment was determined to be 50.1 mJ/m$^2$ ($\gamma_d = 44.5$ mJ/m$^2$, $\gamma_p = 5.6$ mJ/m$^2$). The total surface energy of CF-H increased after oxidation treatment; this is due to an increase of hydrophilic functional groups
FP onto their surface. This provides evidence that the combined effect of double-scaled roughness and low-surface-energy treatment minimizes surface energy.

Lu et al. [110] synthesized CFs and SiCO/carbon composite fibers with average diameters of 120 and 163 nm, respectively, by electrospinning 7 wt% PAN and 5/7 wt% polyureasilazane (PUS)/PAN in dimethylformamide (DMF), respectively, followed by cross-linking, stabilization, and carbonization at temperatures up to 1000°C. The SiCO/CFs exhibited dual superhydrophilicity (absorbing 87.3% water) and superoleophilicity (60.8% decane absorption). The electrochemical properties determined by cyclic voltammetry show that the SiCO/CFs possess better capacitance behaviors than CFs.

Seo et al. [111] fabricated nm-scale carbon structures on CFs with micrometer-scale thickness using the CVD method, where Ni nanoparticles were used as catalysts of nanostructure growth. Polydimethylsiloxane (PDMS) thin films were used to provide hydrophobic surface properties. To adjust the pH value of the aqueous solutions, HCl and NaOH were used for acidic and basic solutions, respectively. For both cases, the initial contact angle measured immediately after dropping 3 μL of liquid droplet was higher than 170°. With increasing contact time to 30 min, the contact angles were almost constant. This implies that the superhydrophobicity of PDMS-coated surfaces can be sustained in a corrosive environment.

Qiu et al. [112] fabricated a superhydrophobic CF layer. CFs with enhanced corrosion inhibition ability were catalytically grown on a Zn surface. Cu was produced by a galvanic replacement reaction, and acted as a catalyst for CF growth. CFs endow the Zn surface with superhydrophobic wettability (~150.5°), enabling it to withstand corrosion by the external environment. The Zn-CF material shows enhanced corrosion resistance (–OH, C=O, and O=–C–O) during the acid oxidation process. On the contrary, the fluorinated CF-FP shows lower surface energy. The decrease of both \( \gamma_L \) and \( \gamma_S^P \) is ascribed to the substitution of the lower energy C–F groups of FP. The total surface free after the growth of GNFs decreased to 11.85 mJ/m\(^2\) (\( \gamma_S^L = 6.45 \) mJ/m\(^2\), \( \gamma_S^P = 5.4 \) mJ/m\(^2\)). This decreased surface free energy is due to the hydrophobic surface of the GNFs. In the case of CF-GNF-FP, the surface free energy decreases significantly after grafting the FP onto their surface. This provides evidence that the combined effect of double-scaled roughness and low-surface-energy treatment minimizes surface energy.

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Table 1. Dispersive (\( \gamma_L^D \)), polar (\( \gamma_L^P \)), and surface free energy (\( \gamma_L \)) components of wetting liquids used in Park’s work: pristine CFs, oxidized CF-H, Ni-doped mesoporous TiO\(_2\) film coated CFs, fluoropolymer coated CFs, GNF coated CFs, and fluoropolymer coated CF-GNF (unit: mJ m\(^{-2}\)).

<table>
<thead>
<tr>
<th>Liquid</th>
<th>( \gamma_L^D ) (mJ m(^{-2}))</th>
<th>( \gamma_L^P ) (mJ m(^{-2}))</th>
<th>( \gamma_L ) (mJ m(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>21.8</td>
<td>51.0</td>
<td>72.8</td>
</tr>
<tr>
<td>Diodimethane</td>
<td>50.42</td>
<td>0.38</td>
<td>50.8</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>31.0</td>
<td>16.7</td>
<td>47.7</td>
</tr>
<tr>
<td>Glycerol</td>
<td>33.9</td>
<td>29.8</td>
<td>63.7</td>
</tr>
<tr>
<td>CFs</td>
<td>44.5</td>
<td>5.6</td>
<td>50.1</td>
</tr>
<tr>
<td>CF-H</td>
<td>44.1</td>
<td>27.3</td>
<td>71.4</td>
</tr>
<tr>
<td>CF-FP</td>
<td>29.5</td>
<td>3.8</td>
<td>33.3</td>
</tr>
<tr>
<td>CF-GNF</td>
<td>6.45</td>
<td>5.4</td>
<td>11.85</td>
</tr>
<tr>
<td>CF-GNF-FP</td>
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<td>3.3</td>
<td>7.7</td>
</tr>
</tbody>
</table>

**CF**: carbon fiber, **GNF**: graphite nanofiber, **FP**: fluoropolymer.
inhibition properties compared with bare Zn because of the air barrier originating from the superhydrophobic nature of the treated surface. The failure process of the superhydrophobic surface was monitored in situ using the open circuit potential technique. The perforations caused by capillary condensation decreased the superhydrophobicity of the surface and diminished its corrosion inhibition efficacy.

4. Superhydrophobicity on CNTs

CNTs, especially those with a cylindrical nanostructure, are of immense research interest for their outstanding behavior in practical applications such as nanotechnology, electronics, optics and other fields of materials science and technology [43,63,90,113-119]. However, in many cases, CNTs wettability and dispensability are crucial factors in their performance; example applications include reinforced polymer composites, templates, sensors, catalysts, electrode, etc. To date, many investigators have endeavored to fabricate CNTs having a superhydrophobic surface.

Previous studies have mostly focused on aligned CNTs films [43,90,117-119]. Zhu et al. [117] fabricated two model surfaces with two-tier scale roughness in a well-controlled manner and compared the superhydrophobicity and contact angle hysteresis of these surfaces with those of microscale rough surfaces by controlled growth of CNT arrays followed by coating with fluorocarbon layers formed by plasma polymerization. A schematic illustration describing surface roughness obtained by the methods investigated in this study is shown in Fig. 6. Fig. 6a is a control (silicon I) surface fabricated by photolithography; Fig. 6b is a schematic representation of CNT arrays grown on silicon wafers, which are denoted as model surface II (WCA: 154-165°); Fig. 6c represents model surface III (WCA: 155-166°), where nanoscale roughness exists in the CNT array grooves. The only difference between surfaces II and III is the nanoscale roughness that exists in the CNT array grooves on surface III. These surfaces are coated with 20 nm fluorocarbon layers that have low surface energy and stabilize the CNT arrays. The CNT array size, pitch, and height have been varied to explore geometric effects on surface hydrophobicity. Compared to patterned Si surfaces with similar geometrical sizes, the nanoscale roughness does not significantly increase the apparent WCA; the microscale roughness thus determines the apparent WCA provided that the microscale roughness dominates the nanoscale roughness. Wong et al. [117] found that the introduction of nanoscale roughness can decrease the contact angle hysteresis to less than 1° and improve the stability of superhydrophobic surfaces. Furthermore, nanoscale roughness can also reduce the strict requirements of microscale roughness design for superhydrophobic surfaces. Introduction of nanoscale roughness on the groove bottom can decrease the microscale array height required for superhydrophobicity. These results improve the understanding of the effects of two-tier roughness on superhydrophobicity and offer additional design approaches for stable and robust superhydrophobic surfaces with self-cleaning properties.

Hong and Uhm [118] prepared superhydrophobic CNTs by low-pressure CF4 glow plasma to provide roughness and fluorination to CNTs. The total surface free energy of CNT powder treated by CF4 plasma for 20 min was calculated to be drastically decreased from 27.04 to 4.06 \times 10^{-1} \text{mJ/m}^2.\ Superhydrophobic CNT powders were prepared by employing CF4 glow discharge plasma to provide roughness and fluorination to CNT powders and water droplets bouncing on CNT powders were observed.

Luo et al. [43] fabricated a new flexible multifunctional CNT/Nafion composite film with superhydrophobicity and high conductivity via a vacuum filtering method. The surface wettability of the nanocomposite film could be conveniently controlled by varying the filtering rate and the content ratio of Nafion to CNT in the composite solution. The films fabricated by filtering a 9.8 wt% Nafion composite solution with filtering rate of 0.5 mL/min exhibited the highest WCA of 165.3 ± 1.9° and the smallest water sliding angle (SA) of 3.3 ± 0.7°. A fatigue test showed that the films retained the superhydrophobicity and the electric conductivity after 1000 bending cycles. The dramatic reduction of the anodic peak potential by the flexible CNT/Nafion nanocomposite films (CNNFs) electrode in cyclic voltammograms of β-nicotinamide adenine dinucleotide (NADH) demonstrates the strong potential of CNNFs in dehydrogenase-based biosensor applications.

It was recently reported that vertically aligned multi-walled CNT (VACNT) films produced by different techniques can present a hydrophobic character [120]. In particular, CO2 laser irradiance was used to modify the CNT surface by decreasing the polar component of the surface energy. Ramos et al. [120] demonstrated the formation of stable superhydrophobic VACNT surfaces prepared through CO2 laser irradiance, where the contact angle value reached 161°. VACNT arrays were synthesized by microwave plasma CVD using N2/H2/CH4. A CO2 laser technique was applied on the VACNT surfaces with irradiance at
different laser powers to promote the stability of the superhydrophobic surfaces. Contact angle measurement revealed that the irradiated VACNT surface is superhydrophobic at all irradiances tested. Unlike as-grown VACNTs, the samples treated with a CO₂ laser showed no sign of water seepage even after a prolonged period of time (~24 h). They also obtained superhydrophobic VACNT films by a microwave plasma CVD method. The values of the WCA changed to 35.7 ± 4.2° and to 142.2 ± 6.5° after CO₂ laser irradiance of 15 KW cm⁻² and 50 KW cm⁻², respectively.

Stimuli-responsive smart surfaces with dynamically tunable wettability have recently received special attention because of their potential applications [121-123]. Yang et al. [121] fabricated various CNTs films with tunable wettability by a one-step spray-coating method without any chemical modification, where the wettability can be reversibly switched between superhydrophobic and superhydrophilic by alternation of UV irradiation and dark storage. The most distinctive characteristic of the film is its tunable wettability in response to UV light. When the CNT film was exposed to UV light for 40 min, the water CA was found to be about 0°; that is, it was switched from superhydrophobic to superhydrophilic. A water droplet can immediately spread out on the surface. After the UV-irradiated film had been in the dark for 24 h, its wettability recovered to the pristine superhydrophobic state (Fig. 6b).

Most of the current strategies for fabricating durable hydrophobic surfaces can provide contact angles close to 170° coupled with icephobicity [32,124]. Zheng et al. [32] presented a simple method to produce CNT-based films with exceptional superhydrophobicity and impact icephobicity by depositing acetone-treated SWCNTs onto glass substrates. This method is scalable and can be adopted for any substrate, both flexible and rigid. These films displayed a high contact angle, in the vicinity of 170°, verified by both static and dynamic analysis processes. Dynamic evaporation studies indicated that a droplet deposited on the treated films evaporated in the constant contact angle mode for more than 80% of the total evaporation time, which is characteristic of superhydrophobic surfaces. Furthermore, the acetone-functionalized films showed a strong ability to mitigate ice accretion from supercooled water droplets (-8°C); the droplets were found to bounce off the films tilted at 30°.

Recently, superhydrophobic transparent conductive films have attracted considerable interest due to their importance in fundamental research and potential industrial applications [48,125-127]. Meng and Park [125] prepared multi-walled CNT (MWCNT) thin films on glass substrates. The prepared films showed transparent, conductive, and superhydrophobic properties. MWCNTs were dispersed in FP solutions for modification of their surface by grafting a FP (Fig. 7). A dip-coating process was used to prepare the films at a continuous speed and different numbers of coatings were applied. Fig. 7 shows schematic diagrams illustrating the changes of the contact angle and the surface properties of the film. As shown in this figure, the water droplet retains an ellipsoidal shape on the MWCNTs with a contact angle of 130°, suggesting the raw MWCNT materials have a hydrophobic character (Fig. 7a). The sharp decrease of the CA from 130° to 41.9° for MWCNT-OH (Fig. 7b) originates from the hydrophilic properties of the fully H₂O₂ treated surface. This is due to an increase of hydrophilic functional groups (~OH, C=O, and O=C–OH) during the H₂O₂ oxidation process [21]. The CA of glass increases to 117.5° after being coated with FP, and this is ascribed to the surface of the glass being coated with densely packed ~CF groups (Fig. 7c). The CA of MWCNTs-OH after treatment with the FP increased to 160.2°, and the surface showed superhydrophobicity (Fig. 7d). The CA was 160.2° even at a transmittance of 83.5% (at 550 nm) and a sheet resistance of 1,38×10⁴ Ω sq⁻¹. This clearly indicates that the networks comprised of MWCNTs increase the conductivity while those containing the FP did not affect the conductivity of the films.

Tang et al. [128] functionalized covalently MWCNTs with polyhedral oligomeric silsequioxane (POSS). A stable and...
**Superhydrophobic Carbon-Based Materials**

Rafiee et al. [131] demonstrated that a surface roughness effect in conjunction with the surface chemistry of graphene sheets can be used to dramatically alter the wettability of a substrate. In order to disperse graphene sheets on a substrate, they performed high-power ultrasonication of graphene sheets in water or acetone. By controlling the relative proportion of acetone and water in the solvent, the contact angle of the resulting graphene film can be tailored over a wide range (from superhydrophobic to superhydrophilic). Such graphene-based coatings with controllable wetting properties provide a facile and effective means to modify the wettability of a variety of surfaces.

Lin et al. [133] prepared a novel superhydrophobic graphene aerogel (GA) with extremely low bulk density and a high WCA. GA offers lower density and simpler processing than other superhydrophobic surfaces developed using vertically aligned CNTs or silica aerogels. They demonstrated that the GA is naturally hydrophobic because of its high surface roughness; following the application of a fluorinated silane, it becomes superhydrophobic with the WCA reaching 160°.

As shown in Fig. 3, fluorinated polymers are commonly used as low surface energy materials; for example, polyvinylidene fluoride (PVDF) is used to produce superhydrophobic materials [134-136]. Zha et al. [135] demonstrated a combined method of solvent exchanging and freeze-drying to fabricate PVDF porous materials that can effectively avoid the skin-layer formation of dried materials. It was observed that the addition of graphene (1 wt%) exerted clear influences on the crystallization, morphol-

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**Table 2. List of graphene-based superhydrophobic surfaces**

<table>
<thead>
<tr>
<th>Method</th>
<th>Method WCA</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Superhydrophobic films</td>
<td>Thermal expansion</td>
<td>–160°</td>
</tr>
<tr>
<td>Conductive, superhydrophobic coatings</td>
<td>Graphene/POSS/CNT</td>
<td>155°</td>
</tr>
<tr>
<td>Aerogels</td>
<td>Fluorinated silane</td>
<td>160</td>
</tr>
<tr>
<td>Porous graphene</td>
<td>PVDF</td>
<td>&gt;150</td>
</tr>
<tr>
<td>PVDF-HFP/graphene microspheres</td>
<td>PVDF</td>
<td>151.6±1.4°</td>
</tr>
<tr>
<td>Graphene/Nafion films</td>
<td>Nafion</td>
<td>–161°</td>
</tr>
<tr>
<td>Biomimetic surfaces-superhydrophobicity, and iridescence</td>
<td>Two-beam laser interference</td>
<td>156.7°</td>
</tr>
<tr>
<td>Mesoporous graphene for separation and absorption</td>
<td>CaCO3: microspheres-hard templates, surface modification-PDMS, CVD</td>
<td>&gt;150°</td>
</tr>
<tr>
<td>White graphenes- nano-rough films</td>
<td>A mixture of boron (B) and boron trioxide (B2O3) powder-precursor</td>
<td>–152°</td>
</tr>
<tr>
<td>Amine functionalized GO films</td>
<td>Alkylamine of varying chain lengths</td>
<td>162°</td>
</tr>
<tr>
<td>Superhydrophobic electroconductive graphene-coated cotton cellulose</td>
<td>Dip-pad-dry method</td>
<td>163± 3.4°</td>
</tr>
<tr>
<td>3D superhydrophobic foams</td>
<td>CVD method</td>
<td>&gt;150°</td>
</tr>
<tr>
<td>Superhydrophobic film as corrosion barrier to copper</td>
<td>Reduced graphene sheets</td>
<td>150.4°</td>
</tr>
</tbody>
</table>


superhydrophobic surface characteristic was observed for the film made of MWCNTs grafted with POSS (MWCNT-g-POSS) even after exposure to a high-humidity environment for three weeks. The WCA of the sample was measured to be 160.5 ± 1.1°. In addition, MWCNT-g-POSS buckypaper exhibited better efficiency in fire retardancy compared to the MWCNT buckypaper. This was due to the smaller median pore size of the MWCNT-g-POSS hybrid buckypaper and char formation during combustion, which could effectively limit the heat and mass transfer and the diffusion of flammable gases and therefore slow down the combustion and degradation of the resin.

### 5. Superhydrophobicity on Graphene

Graphene is a single-atom-thick sheet composed of sp²-hybridized carbon atoms and it exhibits many intriguing properties [48,127-130]. A perfect graphene nanosheet is hydrophobic, but surface treatment or introduction of various functional groups or additional components will remarkably vary its surface properties. Graphene has aroused strong interest in the context of exploring novel functional superhydrophobic surfaces [30]. Several experimental and modeling studies have focused on exploiting micro-scale surface roughness to engineer superhydrophobic graphene. Several research groups have fabricated superhydrophobic graphene surfaces using an irregular stack of graphene oxides (GO) prepared by chemical oxidation of graphite, and pertinent results are shown in Table 2 [131-144].

Rafiee et al. [131] demonstrated that a surface roughness effect in conjunction with the surface chemistry of graphene sheets can be used to dramatically alter the wettability of a substrate. In order to disperse graphene sheets on a substrate, they performed high-power ultrasonication of graphene sheets in water or acetone. By controlling the relative proportion of acetone and water in the solvent, the contact angle of the resulting graphene film can be tailored over a wide range (from superhydrophobic to superhydrophilic). Such graphene-based coatings with controllable wetting properties provide a facile and effective means to modify the wettability of a variety of surfaces.

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ogy, surface area, and wettability of PVDF. PVDF/graphene (1 wt%) porous materials are a superhydrophobic material with a large contact angle (>150°). These properties are due to it being a hybrid porous material composed of strings of roughened nanospheres (250–300 nm) with hierarchical micro-/nano-scaled roughness. On the basis of the Cassie-Baxter model, such multi-level surface roughness is responsible for its superhydrophobicity. Zhang et al. [136] demonstrated the fabrication of hybrid PVDF-hexafluoropropylene (HFP)/graphene composite microspheres through a spontaneous formation process. The addition of graphene to a PVDF-HFP/DMF solution has a strong influence on its gel structure in both the wet and dry states. Morphological characterization by SEM indicates that the dried gel is composed of PVDF-HFP/graphene (0.25 wt% to PVDF-HFP) microspheres with a size distribution of 8–10 μm. The contact angles of pure PVDF-HFP and PVDF-HFP/graphene are 132.7 ± 2.7° and 151.6 ± 1.4°, respectively. This superhydrophobicity is due to the PVDF-HFP/graphene gel being composed of microspheres with nanoscaled surface roughness.

Usually, the micro-/macro-scale surface structures of functional films strongly affect the critical properties, such as wetting, and they should exhibit super water repellency with a WCA larger than 150° for self-cleaning and antimicrobial surfaces. Choi and Park [137] demonstrated superhydrophobic thin films of graphene-based materials induced by a hierarchically petal-like structure. The superhydrophobic graphene/Nafion nano hybrid films were prepared by controlling the structures with respect to the chemical composition from an interpenetrating networked and compactly interlocked structure (specific surface area of 9.56 m²/g) to a hierarchical petal-like, porous structure (specific surface area of ~413 m²/g). The hybrid films revealed a petal-like, porous structure with hierarchical roughness, where macroscale roughness was produced in the lateral direction of the hybrid sheets while nanoscopic roughness was created on the edges of the hybrid sheets. The surface morphologies of the hybrids were changed with respect to the amount of Nafion and their CAs increased from ~97° to ~161° with increasing Nafion content.

Shammugharaj et al. [141] demonstrated a facile method for the synthesis of amine functionalized GO films using alkylamines of varying chain lengths. Alkylamines consisting of hydrophobic long chain alkyl groups and hydrophilic amine groups were chemically reacted to the GO surface via two types of reactions viz. 1) An amidation reaction between amine groups and carboxyl acid sites of GO, and 2) a nucleophilic substitution reaction between amine and epoxy groups on the GO surface. Alkylamine-modified GO surfaces showed enhanced roughness, and this effect was more pronounced with increasing amine chain length. WCA measurements revealed that the hydrophobic nature of graphene depended on the chain length of the grafted alkylamines, and this may be corroborated to a decrease in the surface energy values. Grafting of long chain alkylamines such as hexadecylamine or octadecylamine on the GO surface followed by thermal reduction resulted in the formation of superhydrophobic surfaces with WCA values of 152° and 162°, corroborating the role of alkylamine chain length in superhydrophobic wetting control of a thermally annealed GO surface.

Singh et al. [143] used Teflon coated graphene building blocks to create a superhydrophobic structure with an ordered pore structure of ~200 μm in dimension. The advancing WCA on the foam surface exceeded 163°. The graphene foam inherits the pore structure of the Ni foam template used in the CVD growth process. This method can be used to uniformly tune the pore size and structure of the graphene foam by selecting the appropriate Ni foam template. The graphene foam can store elastic strain energy as it is deformed by the impacting drop and then deliver it back to the drop, which could assist the rebound process.

6. Superhydrophobicity on Other Carbons

There has been a continuous growth of interest throughout the world in synthesizing porous carbons to fabricate superhydrophobic films, in addition to CFs, CNFs, CNTs, and graphene. A typical method to control the wettability of a solid is surface modification with low surface energy materials. Superhydrophobic surfaces can then be fabricated successfully with micro- or nanostructured surfaces. As an environmentally benign and economically viable optoelectronic device material, superhydrophobic amorphous carbon films are of interest in various applications [35,145-147].

Zhou et al. [35] prepared amorphous carbon films with a nanostructured surface and deposited the films on silicon and glass substrates at different substrate temperatures through a magnetron sputtering technique. The pure carbon films exhibited different wettability, ranging from hydrophilicity with WCA less than 40° to superhydrophobicity with a WCA of 152°. This reveals that the surface wettability of WCA films amorphous carbon films can be controlled well by using nanostructures with various geometrical and carbon state features. The graphite-like carbon film deposited at 400°C without any modification exhibited super-hydrophobic properties, due to the combination of microstructures of spheroids with nanostructures of protuberances and interstitials.

Li et al. [145] demonstrated that the wettability of a Pt/carbon/Nafion catalyst layer in proton exchange membrane fuel cells is critical to their performance and durability, especially with respect to the cathode, as water is needed to transport protons to the active sites and is also involved in deleterious Pt nanoparticle dissolution and carbon corrosion. They used the water droplet impacting method to determine the wettability of 100% Nafion films as a benchmark, and then prepared Vulcan carbon (VC)/Nafion composite films. Spin-coating in a Pt-free state was used for both cases. The wettability of the VC/Nafion composite films depends significantly on the VC/Nafion mass ratios, even though Nafion is believed to be preferentially oriented (sulfonate groups toward VC) in all cases. At low VC contents, a significant water droplet contact angle hysteresis is seen, similar to pure Nafion films, while at higher VC contents (>30%), the films become hydrophobic, also exhibiting superhydrophobicity, with surface roughness playing a significant role. At VC contents higher than 80% VC, the surfaces become wettable again as there is insufficient Nafion loading to fully cover the carbon surface. It is thus possible to calculate the Nafion:carbon ratio required for full coverage of carbon by Nafion.

Banerjee et al. [146] synthesized highly porous activated
carbon with a large surface area and pore volume by KOH activation using commercially available activated carbon as a precursor. By modification with PDMS, highly porous activated carbon showed superhydrophobicity with a WCA of 163.6°. The changes in wettability of PDMS-treated highly porous activated carbon were attributed to the deposition of a low-surface-energy silicon coating onto activated carbon, which had microporous characteristics. Using a facile dip-coating method, superhydrophobic activated carbon-coated sponges were also fabricated. The sponges exhibited excellent absorption selectivity for the removal of a wide range of organics and oils from water, as well as recyclability, thus showing potential as efficient absorbents for the large-scale removal of organic contaminants or oil spills from water.

7. Summary

Carbon is a versatile material due to its porosity, conductivity, thermal conductivity, wide operating potential range, high chemical stability, and reasonable cost. In this review, we have presented different techniques for the preparation of superhydrophobic carbon-based materials such as CFs, CNFs/CNTs, graphene, amorphous carbons, and porous carbons. These superhydrophobic carbon-based materials hold great promise for the development of various industrial products. Overall, there are two traditional methods to control superhydrophobic surfaces: 1) surface micro-scale roughness; and 2) low surface energy materials treatment. Several technologies that can improve surface roughness and decrease surface energy have been developed, including thermal treatment, chemical modification with -(CH$_2$)$_n$-CH$_3$, or -(CF$_2$)$_n$-CF$_3$ groups containing materials, CVD method, plasma treatment, an electro-spinning. From a commercial point of view, carbon-based superhydrophobic materials can be applied to smart surfaces with tunable wetting behavior in different stimuli-responsive environments. They have attracted considerable attention for applications in self-cleaning surfaces, anti-adhesive coatings, biosensors, microfluidics, and many other areas.

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