New insights into hydrophobicity at nanostructured surfaces: Experiments and computational models

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Abstract
This review deals with different aspects of hydrophobicity at nanostructured surfaces. Theoretical and geometric effects as well as those of surface feature geometry on hydrophobicity are explored in this article. This review includes surface modification methods used to change surface hydrophobicity and effect on adhesion of cells as nano substrate. A small chapter is devoted to hydrophobicity at self-assembled monolayers as a special type of nanostructured surface. To the different models describing hydrophobicity is devoted one up to dated chapter. Calculation methods including quantum, density functional theory, and molecular modeling bring novel perspectives to the study of hydrophobicity at nanostructured surfaces.

Keywords
Nanostructured, surface, hydrophobicity, computational models

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Introduction
Phenomena associated with wetting create an overlap of many disciplines. It is one of the subjects of surface chemistry studies, where it has the key importance in determining surface properties originating from the nature of intermolecular interactions. Huge effort is put into the modification of surface chemistry of various solid surfaces to obtain the desired hydrophobicity.¹⁻³ Surface hydrophobicity is also a fundamental property of solid surfaces that play important roles in household, industrial, and advanced applications.⁴ A myriad of various methods exist which are intended to modify surface wettability⁵⁻⁷ in the desired way. Surface wettability is influenced by many features, such as the chemical heterogeneity of the surface, its asperity, and disposition of surface structures, and in the case of atomically flat surfaces, it is also influenced by the values of Miller indices.⁸⁻¹¹ Hydrophobicity is one of the key attributes of advanced microelectronics, acting as a safeguard for electronic devices that prevents them from undergoing corrosion, hygroscopic swelling, and more importantly, preventing metal surfaces from oxidation, thereby increasing the lifetime of the material. Hydrophobic materials are currently considered to be one of the most prominent and efficient materials for academic and industrial purposes due to their numerous advantages, which

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include self-cleaning, drag reduction, anti-biofouling, and corrosion resistance. To enhance the reliability and stability of these types of microelectronics, usage of moisture-resistant materials in humid environments is needed. Hydrophobicity has fascinating characteristics for electronic applications, which include the ability to extend the life span of electronic materials and the ability to sustain their properties especially in a humid environment. Highly hydrophobic coatings have been of particular interest over the last decade due to their extensive potential applications in anti-corrosion, self-cleaning, anti-fouling, anti-icing, and drag-reducing materials in a wide range of industries. This article deals with novel aspects of hydrophobicity. The most common models describing solid–liquid interface are explained. This article deals with impact of surface geometry on surface hydrophobicity and adhesion on nanostructured surfaces. Finally, the surface hydrophobicity also arises from intermolecular interactions within liquid–solid interface, which will be mentioned. New insight to hydrophobicity brings different ways of computational models.

Theoretical background of hydrophobicity at nanostructured surfaces

When a drop of liquid is placed on a flat solid surface, it will form a spherical cap. An angle where liquid, vapor, and solid meet is the static contact angle $\theta$. Young’s equation is a representation of intermolecular forces at equilibrium among three interfaces, which meet at triple line

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV}\cos \theta$$

(1)

where $\gamma_{SV}$, $\gamma_{SL}$, and $\gamma_{LV}$ denote the solid–vapor, solid–liquid, and liquid–vapor surface tension, respectively. For a water drop, when the contact angle is less than 90°, the surface is considered hydrophilic. Between 90° and 150°, the surface is hydrophobic. If the water contact angle is greater than 150°, the surface is considered superhydrophobic. However, the largest water contact angle $\theta_f$ reported for smooth solid surfaces is about 120°. Most of the nonpolar surfaces are hydrophobic compared to the polar surfaces, which is usually attributed to the weak adhesion work. Partial wetting occurs when a liquid drop is surrounded by a microscopically thin film adsorbed at the surface. Complete wetting corresponds to a macroscopically thick layer of liquid on the surface of solids. When considering a volatile liquid drop on the solid, thermodynamic equilibrium is reached in a relatively short time. A solid surface in the vicinity does not remain dry but establishes contact with the saturated vapor phase and is covered by a (sub)monolayer of adsorbed liquid molecules. Thus, liquids with eligible volatility are suitable for contact angle measurements and surface energy calculations. A static contact angle of more than 120° is almost impossible to achieve on the flat solid surface. To reach strong hydrophobicity, there is a need to combine chemically hydrophobic materials and surface patterning. For example, lotus leaves are known to be superhydrophobic and self-cleaning due to the hierarchical multiscale roughness of their leaf surfaces. The self-cleaning phenomenon is thus widely known as the “lotus effect.”

When mechanical or chemical surface inhomogeneities or surface patterning are being considered, Young’s equation needs to be modified. Mechanical inhomogeneities carried into Young’s equation lead to the derivation of the Wenzel model. In the case of the chemical surface, inhomogeneities are being considered—the Cassie model is derived. Derivation procedures of mentioned wetting models are given in Shirtcliffe et al. These two models describe two possible wetting regimes or states: the homogeneous (Wenzel) and the composite (Cassie–Baxter) regimes. The Wenzel model describes wetting, where the liquid droplet is in contact with the peaks and valleys of the rough surface with the following equation

$$\cos \theta_W = R_f \cos \theta_y$$

(2)

where $\theta_W$ is the Wenzel contact angle and $R_f$ is the roughness factor, which is defined as the surface area ratio between the rough surface and its projection on a 2D plane. The Cassie–Baxter model describes chemically heterogeneous wetting, where the liquid drop on the solid is carried by the projections of solid structure and does not penetrate into the liquid phase, while trapped air is another part participating in chemical heterogeneity. The Cassie–Baxter equation can be derived from Cassie’s law, describing wetting for a two-component surface

$$\cos \theta_C = f_1 \cos \theta_1 + f_2 \cos \theta_2$$

(3)

where $f_1$ is the area fraction of the solid surface in contact with the liquid droplet and $\theta_1$ is the contact angle of the liquid droplet according to Cassie. In this case, increasing the area fraction of air $1 - f_1$ will increase the contact angle and reduce the adhesion of the liquid droplet to the surface; thus, the surface is “slippery” and low contact angle hysteresis is achieved. Cassie’s contact angle can be also expressed as follows

$$\cos \theta_c = \frac{1}{S_{SL}} \iint_{S_{SL}} \cos(\theta)(x,y) \, dx \, dy$$

(4)

where $\theta_C$ is Cassie’s contact angle, $S_{SL}$ is the interface area, and $x$ and $y$ are spatial coordinates. Relation between a critical value of $f$, below which the Cassie regime exists and above which the Wenzel regime is thermodynamically more stable; surface roughness $R_f$, and the corresponding transition critical wetting angle ($\theta_c$) can be defined by
\[
\cos \theta_c = \frac{f - 1}{R_f - f}
\]  

(5)

For the stability of the Cassie–Baxter state, factors such as Laplace pressure and drop internal hydrostatic pressure are responsible. As it is shown in equation (6), Laplace pressure depends mainly on the liquid surface tension and surface featured geometry. The pressure difference across the liquid–vapor interface is given by the Laplace equation. A decrease in the distance between the surface features decreases the radius of curvature and leads to an increase in the total pressure the structure can support.\textsuperscript{21} Morikawa et al.\textsuperscript{22} present a relatively simple way for Laplace pressure measurement in a microfluidic channel. For Laplace pressure applies

\[
P_L = \gamma \left(\frac{\cos \theta + \cos \theta^*}{d} + \frac{2\cos \theta}{w}\right)
\]  

(6)

where \(\gamma\) is the used liquid surface tension, \(\theta\) is the contact angle on the flat surface, \(\theta^*\) is the contact angle on the nanostructured surface, and \(d\) and \(w\) are the depth and width of a used microfluidic channel. The exact value of the Laplace pressure can be obtained by the measurement schematically shown in Morikawa and Tsukahara. As previously mentioned, Cassie–Baxter’s state is stable only when the following condition is met

\[
P_c = \frac{\gamma f \cos \theta_{\text{liquid}}}{(1 - f)A/L}
\]  

(7)

where \(\gamma\) is the liquid–air surface tension and \(A\) and \(L\) represent the cross-sectional area and perimeter of the pillar. \(P_c\) represents the critical value of the Laplace pressure needed to preserve air pockets. \(P_c\) acts against the internal hydrostatic pressure. Gravity is responsible for the internal drop pressure, expressed as

\[
P_i = \frac{V \rho g}{A_{\text{contact}}}
\]  

(8)

In the case of a liquid drop with volume \(V\) and apparent contact angle \(\theta\), the interface area equals to

\[
A_{\text{contact}} = \pi \left\{ \frac{6V}{\pi (1 - \cos \theta) (3 \sin^2 \theta + (1 - \cos \theta)^2)} \right\}^{\frac{1}{2}}
\]  

(9)

The differences between internal hydrostatic pressure and Laplace pressure are responsible for the intensity of drop pinning shown in Figure 1(e) and (f). Figure 1(e) shows the state of adhesive hydrophobicity, strong pinning, and high contact angle hysteresis. Figure 1(f) shows the opposite—state of anti-adhesive hydrophobicity, weak pinning, and low contact angle hysteresis. In the case of inhomogeneous wetting (Figure 1(b)), Cassie–Baxter’s and Wenzel’s regions can alternate. Superhydrophobicity can be achieved in the following ways: surface roughness alone, surface roughness and surface chemical modification with low surface energy material, and co-deposition of hydrophobic particles with a metal matrix.\textsuperscript{15} Roy et al. developed a force balance analytical model for designing superhydrophobic surfaces using micro texturing. The superhydrophobicity has been reached at pillar size of 30 \(\mu\)m.\textsuperscript{24} Extreme hydrophobicity has been presented by Zhang et al.\textsuperscript{25} They introduced hydrophobic metal assembly, which traps an amount of air sufficient to keep the assembly floating on water. Generally, both the surface chemistry and the surface roughness affect hydrophobicity, and the interplay between these properties has been the subject of active research during the last decades. We have prepared a nanostructured metal polymer hydrophobic material by the combination of electrochemical deposition and the spin-coating method easily, where the hydrophobicity was enhanced by a thin polymer layer and the Wenzel model has been applied.\textsuperscript{26} In another work, we have prepared a hydrophobic silver dendritic particle layer with fractal geometry by pulse electrodeposition, where the Cassie–Baxter model has been applied.\textsuperscript{27} We have also focused on the

![Figure 1](image-url)

Figure 1. Various models of liquid–solid interface and impact of solid nano/micro surface structuring. Wetting according to Young (A), inhomogeneous wetting (B), wetting according to Wenzel (C), and the penetrating Cassie–Baxter model (D). The Cassie–Baxter wetting regime with strong pinning (E), weak pinning (F), and with hierarchical aligned structure (G).
The effect of surface hydrophobicity and specifically to endow the surface with nano-scale roughness, such as etching and lithography, sol-gel processing, and electrospinning, have been implemented, while the surface chemistry has been modified by using strategies involving physical and chemical adsorption. The self-cleaning of a lotus leaf is ascribed by two criteria: the hierarchically combined micro- and nano-scaled structure (schematically shown in Figure 1(g)) of the surface (physical factor) and the low surface tension compound covered on the surface (chemical factor). The bouncing behavior depends on the surface’s hydrophobic property. The water repellency of a solid surface is quantified by the restitution coefficient and contact time of water droplets of various sizes bouncing off the surface as a function of their impact velocity. The restitution coefficient, $\alpha = (v_f/v_0)$, where $v$ and $v_0$ are the water drop velocities before and after the impact, respectively, can be measured from the recorded video images. The way in which a water drop deforms during its impact on a highly hydrophobic solid depends mainly on its impinging velocity, the dimensionless Weber number, $We = (\rho v^2 r / \gamma)$, which compares the kinetic and surface energies of the drop, where $\rho$ and $\gamma$ are the liquid density and surface tension, respectively. The larger the value of $We$ is, the greater the deformation will be. Recently, Marmur and de Lazzer et al. have extended these basic theories to other geometries, environmental conditions, and separation distances while more accurately describing the meniscus and its effect on adhesion.

The effect of surface hydrophobicity and specific surface groups on the onset of capillary force has also been subject to direct measurement recently. Super-oleophobic surfaces have been achieved by using fluoro-decylpolyhedral oligomeric silsesquioxanes (POSS) coatings, which display contact angles greater than 160° for various nonpolar fluids. Boruva and Neumann modified Young’s equation to consider the three-phase contact line tension

$$\cos \theta'_f = \cos \theta_f - \frac{\tau K}{\gamma_{LV}}$$

(10)

where $\tau$ the contact is line tension and $K$ is the curvature. The Lippmann–Young equation accurately predicts the equilibrium contact angle in electrowetting until saturation of the contact angle occurs

$$\cos \theta'_y = \cos \theta_y + \frac{\varepsilon_0 e U^2}{2d\gamma_{LV}}$$

(11)

where $\varepsilon_0$, $\varepsilon$, $U$, and $d$ are the electric permittivity in a vacuum, the dielectric constant, the applied electric potential, and the dielectric layer thickness, respectively.

Whyman et al. derived the contact angle hysteresis model based on a simple thermodynamic model

$$\theta_a - \theta_r = \left( \frac{8U}{\gamma_{LV}R_0} \right)^{1/2} \left( \frac{\cos \theta_a}{\gamma_{LV}} \right)^{1/2} \left( \frac{2 + \cos \theta_a}{2 \gamma_{LV}} \right)^{1/4}$$

(12)

where $\theta_a$ is the apparent contact angle at equilibrium, $\theta_r$ is the advancing contact angle, $\gamma_{LV}$ is the surface tension at the liquid–vapor interface, and $r$ is the initial drop radius. Another theory that allows determining apparent surface free energy is that proposed by Chibowski. Having measured the advancing $\theta_a$ and receding $\theta_r$ contact angles of probe liquids and their surface tension $\gamma_{LS}$, the apparent surface free energy $\gamma_{SV}$ has been calculated from the contact angle hysteresis using the following equation

$$\gamma_{SV} = \frac{\gamma_{LV}(1 + \cos \theta_a)^2}{2 + \cos \theta_r + \cos \theta_a}$$

(13)

When the contact angle hysteresis is known, the liquid drop adhesion force can be calculated using simple equation

$$F = \gamma_b (\cos \theta_r - \cos \theta_a)$$

(14)

Contact angle measurements are widely employed in the studies of wetting and dewetting of the surfaces. There are no fully comprehensive rational considerations as the surface switches from hydrophilic to hydrophobic in case of contact angle change from 89° to 91°. Benedict et al. asked whether the liquid drop contact angle correlates with adhesion. This question still remains to be fully clarified. They have also shown the almost linear correlation between the adhesion force and the receding contact angle which has changed how we see the correlation among hydrophobicity, contact angle, and adhesion.

Gao and McCarthy highlighted the importance of the three-phase contact line. They also suggest that one has to know the limitations of Wenzel and Cassie–Baxter theories.

The surface energy $\gamma_S$ of the silane self-assembled monolayer (SAM) can be determined using the Good–Girifalco equation together with Young’s equation for the equilibrium contact angle

$$\gamma_{SV} = \frac{\gamma_{LV}(1 + \cos \theta)^2}{4}$$

(15)

The surface energy is inversely proportional to the contact angle values, so it is higher for lower contact angle values and lower when the contact angle is higher. Forces by which the surface hydrophobicity is driven are van der Waals and electrostatic forces. They are responsible for the level of surface hydrophobicity. Long-ranged van der Waals forces can reach the distance of few tens molecules (diameter), proved by AFM microscopy and theoretical
methods such as molecular dynamics. The wetting behavior of surfaces is believed to be affected mainly by van der Waals forces; however, there is no clear demonstration of this.\(^3\) To predict intermolecular van der Waals-based adhesion interactions, fundamentally through the surface-based approach, methods such as Johnson–Kendall–Roberts or Derjaguin–Muller–Toporov adhesion theory can be used.\(^3\) The interactions mostly originated from Van der Waals forces for nonpolar liquids and hydrogen bonds for polar liquids such as water.\(^4\) The ideal interaction between a surface and a liquid is dictated by surface forces. Surface forces can be subdivided into three components: van der Waals forces, which exist at any interface between solids and liquids; electrostatic interactions, which exist between charged or polar surfaces and fluids; and structural forces, principally hydrogen bonding. These interactions influence the wetting behavior and determine whether the interaction with water is hydrophilic or hydrophobic, control the electronic structure at the liquid–solid interface, influence the frictional interaction, and modulate the chemical activity. However, this ideal picture of the surface interactions is complicated when considering surface heterogeneities, including roughness and contamination, which interfere with the formation of an equilibrium configuration between the liquid and the surface, leading to eccentric behaviors, including superwetting, superslipping, and superhydrophobicity.\(^5\) Graphene demonstrates long-range \(\pi\) conjugation, resulting in unique surface and chemical properties. For example, graphene interacts with molecules that are weakly adsorbed on its surface by donating or accepting charge carriers, resulting in a modulation of carrier concentration or doping,\(^6\) even though the van der Waals forces are known to promote the “self-cleaning” of interfaces.\(^7\) The long reach of van der Waals force can be demonstrated by the work of Rai et al. where the van der Waals force can influence the hydrophobicity of the top layer through five graphene layers. This van der Waals transparency can be reached on copper, gold, and silicon.\(^8\) Equation (16)\(^9\) provides an expression of the van der Waals interaction intensity

\[
E_{VDW} = -\frac{k\pi\rho_1\rho_2}{12r^2}
\]  

where \(k\) is the constant of the atom–atom pair potential, \(\rho_1\) and \(\rho_2\) are the numbers of atoms per unit volume at the interface, and \(r\) is the separation distance between the two surfaces. The form of the Lennard–Jones potential approximates the van der Waals potential and its common definition is

\[
U_{LJ} = 4\varepsilon_{ij} \left[ \left( \frac{R_{\text{min}}}{r} \right)^{12} - \left( \frac{R_{\text{min}}}{r} \right)^6 \right]
\]  

where \(\varepsilon_{ij}\) and \(R_{\text{min}}\) are the characteristic energy and the van der Waals radius, respectively. The distance between a pair of atoms is represented by \(r\).\(^10\)

**Figure 2.** Schematic representation of hexagonally oriented features on the planar surface mentioned in Figure 3.

**Geometrical aspects of hydrophobicity at nanostructured surfaces**

As smaller and smaller surface patterns are created on the micrometer or nanometer scale, one must ask whether the corresponding wetting structures can be understood using the same theoretical framework as appropriate for the macroscopic scale, a question which is of fundamental interest to the science of colloids and interfaces.\(^2\) It has also been suggested that the so-called two-tiered hierarchical roughness, composed of the superposition of two roughness patterns with different lengths, and fractal roughness may enhance superhydrophobicity.\(^3\) Hexagonally ordered features (Figure 2) can also enhance hydrophobicity by strong pinning (Figure 3).\(^4\)

Since hydrophobic surfaces do not favor the formation of a hydrogen bond network with water molecules, they orient themselves to minimize the area of contact with such surfaces, which are therefore not wetted by water.\(^5\) A silicon hexagonally ordered nanorod array prepared by Zi-Wen et al.,\(^6\) where the Cassie model was adopted, shows a contact angle of 142\(^\circ\). For hexagonal geometry, the \(f_s\) value is defined as

\[
f_s = \frac{\sqrt{3}\pi d^2}{6a^2}
\]  

where \(d\) is the nanorod diameter, and \(a\) refers to the distance of nanorod midpoints and \(a\) is the nanorod separation distance. In a hydrophobic surface modification, the character of the nanorod tip has to be considered.
Therefore, a composite interface is desirable for superhydrophobicity and self-cleaning. Surface geometry can provide extreme hydrophobicity and water contact angle enhancement from 70° up to 178°.48 A detailed view of the liquid–solid interface in the Cassie–Baxter state is shown in Figure 4. Authors used the vectors $m$ and $n$ to describe the internal contact angle. Transition prediction between Wenzel and Cassie–Baxter is shown in Figure 5.

The formation of a composite interface is a multiscale phenomenon that depends on the relative sizes of the liquid droplet and roughness details. A composite interface is fragile and can be irreversibly transformed into a homogeneous interface.18 A stable composite interface is then essential for the successful design of superhydrophobic surfaces. However, a composite interface is fragile, and it may transform into a homogeneous interface. To calculate
the contact angle for the composite interface with fractal geometry, Wenzel’s equation can be modified by combining the contribution of the fractional area of the wet surface and the fractional area of air pockets (\(\theta = 180^\circ\)) \(^{18}\)

\[
\cos \theta = R_f \cos \theta_0 - f_{LA} (R_f \cos \theta_0 + 1) \tag{19}
\]

where \(f_{LA}\) is the fractional flat geometric area of the liquid–air interfaces under the droplet. According to the equation, even for a hydrophilic surface, the contact angle increases with an increase in \(f_{LA}\). At a high value of \(f_{LA}\), a surface can become hydrophobic. However, the value required may be unattainable or the formation of air pockets may become unstable. Using the Cassie–Baxter equation, the value of \(f_{LA}\) at which a hydrophilic surface could turn into a hydrophobic one is given as \(^{18}\)

\[
f_{LA} \geq \frac{R_f \cos \theta_0}{R_f \cos \theta_0 + 1} \text{ for } \theta_0 < 90^\circ \tag{20}
\]

Hydrophobic surfaces can be achieved above a certain \(f_{LA}\) value as predicted by equation (20). When the separation distance between nanostructures is about to change continuously, the Cassie–Baxter and Wenzel regime transition can be observed, and a threshold value can be found (Figure 6). A similar experiment where the separation distance is changed is presented in Li et al. When the elastic nanostructured film was stretched, the distance between nanostructures changed and wetting regime transition occurred.

Goel et al. \(^{50}\) observed the highest contact angle (CA) \(\theta_a = 154.8^\circ\), whereas \(\theta_b = 118^\circ\), resulting in the wetting anisotropy (\(\Delta \theta\)) (Figure 7) of about \(a = 37^\circ\). The degree of wetting anisotropy is defined as \(\Delta \theta = \theta_a - \theta_b\).

Marmur \(^{51}\) shows conditions between the Wenzel and Cassie–Baxter states, where a part of the water droplet permeates the space between the structures. Milne and Amirfazli \(^{44}\) describe some examples in which the Cassie equation cannot predict the contact angle. While static contact angles affect dynamic hydrophobicity, the contact angle hysteresis has been used to evaluate dynamic hydrophobicity which is related to the difference between the advancing and receding contact angles. \(^{44}\) The relationship between surface roughness and apparent contact angle (\(\theta_A\))
can be described by the Koch curve fractal formula:
\[
\cos \theta_A = f_1 \frac{L}{l}^{D/2} \cos \theta - f_2, \text{ where } f_2 \text{ is the fraction of the air surface under the water droplet, and } f_1 + f_2 = 1.
\]
\( L \) and \( l \) are the upper and lower limit scales of the surface, respectively, and \( D \) is the fractal dimension. Surface roughness and apparent contact angle have close ties to the value of \( L/l \).52

**Adhesion at nanostructured surfaces and hydrophobicity**

The interaction of cells and tissues with artificial materials designed for applications in biotechnologies and in medicine is governed by the physical and chemical properties of the material surface. There is optimal cell adhesion to moderately hydrophilic and positively charged substrates.53 The interfacial properties of materials govern the performance of biomaterials because cells are in direct contact with the surfaces of materials. Therefore, one of the commonly used approaches to improve the performance of biomaterials is surface engineering, where a material’s surface properties can be modified by chemical and physical means.54 It has been shown repeatedly that cell adhesion to artificial material depends strongly on the physicochemical properties of the material surface, its chemical composition, polarity and wettability, zeta potential, and consequently, the character of the cell–material interaction.53 The surface charge can also change cell behavior through chemical functional groups.55 It is known that cells explore their microenvironment through surface receptors such as integrins. When integrin molecules bind to extra cellular matrix molecules, they recruit various focal adhesion molecules, including vinculin, paxillin, and talin, among others, to form sub-micrometer scale focal complexes.54 Consequently, the findings emphasize the importance of selecting optimal culture conditions to yield a desirable cellular outcome.56 Extracellular matrices may control cellular signaling processes and cell fate via interdependent effects of their micro and nanotopography, as well as on their biochemical molecular structure.57 Water drop adhesion on to the adhesive and anti-adhesive surface is shown in Figure 8.

The concept of hydrophobicity has long been used to explain many natural and synthetic phenomena and processes such as dissolution of inert gases in water, protein folding, colloidal stability, micelle formation, and nanoparticle aggregation.59–63 At the macroscopic level, the degree of hydrophobicity is generally assessed by measuring the droplet contact angle.64 It has been shown that the surface topography has such a significant influence on the hydration behavior that only by controlling the topography of the solute surface can one create a dry, wet, or oscillatory (with time) wet–dry state of the intersolute region.64 Besides, contributions of these different parameters to the manifestation of hydrophobicity have been studied by separating geometry or topography from chemistry that determines the hydrophobic/hydrophilic nature of an engineered protein surface.64 The increase in the compressibility of water near a hydrophobic surface has already been observed for a self-assembled monolayer—water, and protein–water interfaces.64 Moreover, the positively charged surfaces significantly influence cell proliferation and spreading, especially in the early stages of cell response. Positive charges activate the signaling cascade of the immune system and the regenerative response to the biomaterial.65 These surfaces can also be used in energy conversion and conservation. Condensation of water vapor from the environment and/or processed liquid film can form menisci, leading to high adhesion in devices requiring

**Figure 8.** Comparison of adhesive surface water drop pinning (A) and the “non-sticky” antiadhesive superhydrophobic surface (B). Reprinted with permission from Yang et al. Copyright © 2016 Nature.
relative motion. Superhydrophobic surfaces are needed to minimize adhesion between a surface and liquid. Adhesion of a liquid droplet to a surface can be related to the contact angle hysteresis, $\Delta \theta$. Contact angle hysteresis is the difference between the advancing contact angle $\theta_a$ and the receding contact angle $\theta_r$. It is widely reported that a hydrophilic surface could boost biological cell adhesion and activity better. Consequently, many polymers used for tissue engineering are hydrophobic in their native state and require surface modification before cell seeding.

**Self-assembled surface modification for adhesion**

In general, some surface molecules can reversibly switch their chemical conformation or polarity to external stimuli, which causes a change of surface energy, and consequently induces a change of surface wettability. These smart surfaces have some interesting properties. They can reversibly switch between superhydrophobicity and superhydrophilicity for several cycles. These switches often adopt the transitional Wenzel/Cassie superhydrophobic state owing to the bistable state of the responsive materials. Some of the surfaces are sensitive to only one kind of stimuli, while others are responsive to two or three stimuli. Although the surface can remain hydrophobic, the alteration of the surface-wetting state influences the dynamic motion of the droplet. The reversible hydrophobic surface characteristics allow the substrates to be used in many applications such as textiles and sensors. In addition, highly stretchable and hydrophobic surfaces can open the door for new approaches toward tunable photonic system design and self-cleaning applications. The pH-responsive superhydrophobic coating can be applied in controlled selective oil–water separation. The water contact angle (WCA) of pH-responsive coating reaches more than 150° in both neutral and alkali environments. After the acidic treatment, the coating transitions to a superhydrophilic state because of the protonation of the responsive monomer poly-(2-(dimethylamino)ethyl methacrylate). V$_2$O$_3$ thin films are well-known “smart” materials due to their reversible wettability under UV irradiation and dark storage. Their surfaces are usually hydrophobic and turn hydrophilic under UV irradiation. Among them, the stimuli response surfaces with reversibly controllable wettability are particularly interesting due to their potential applications in the study of water motion, microfluidic devices, smart membranes, and sensors. The exogenous stimuli include visible light or UV irradiation, heat, pH or specific solvents, electric field, and mechanical forces. TiO$_2$, WO$_3$, ZnO, CNT, Fe$_2$O$_3$, and V$_2$O$_3$ are well-known photosensitive materials, whose wettability could switch between hydrophobicity and hydrophilicity through UV irradiation and dark storage. Zhang et al. show that air absorption is the main factor causing the film surface to change from superhydrophilicity to hydrophobicity. The application of a voltage to a surface can change the chemical properties as well as the wettability. This process is referred to as electrochemical switching. One subset of electrochemical switching is an electrically induced change in the redox state. When the potential is withdrawn, the active surfactant groups are reduced, thus restoring the surface hydrophobicity. A large variety of external stimuli can trigger changes in surface hydrophobicity and surface energy. Current research has been discussed and categorized according to the types of stimuli, which include electrical, electrochemical, photonic, thermal, mechanical, and environmental effects. Several characteristics are likely to influence the development of intelligent surfaces and devices incorporating these surfaces. The most important factor is the magnitude of the hydrophobicity-changing stimulus. The kinetics, and the reversibility of surface wettability switching, and the long-term surface stability are also important. In the case of adsorption, its uniformity, specificity, adsorbed molecule conformation change, and release is driven by hydrophobicity. Hydrophobic behavior was observed by two silver sputtered films with various roughness from 3 to 33 nm thick were prepared by Dutheil et al. When the non-continuous layer was prepared, hydrophilic behavior was observed. Surface energies of the low silica aerogels were modified by Parvathy Rao et al. using various surface modification agents. They obtained states of superhydrophobicity and water drop contact angle of 154°. Kurusu et al. reviewed the techniques of electrospun fiber mat surface to obtain desired hydrophobicity. The fabrication method for biologically inspired surfaces made of copper oxide was proposed by Zhang et al. where the static contact angle ranged from 17° to 95°. Electrochemical preparation of silver dendritic superhydrophobic films was presented by Guo et al. Thickness of prepared films were about 10 μm. After forming n-dodecathiol SAM, a contact angle of 154° was reached. Graphene films with high hydrophobic and adhesive performance were also fabricated in two simple steps: chemical exfoliation of natural flake graphite following redox and film formation by suction filtration without any chemical modification. The obtained graphene surface showed a controllable WCA change from 0° to 160°. Highly hydrophobic polystyrene-based coating functionalized by organo-modified nanosilica particles by Regalaro et al. They have confirmed strong influence of the organic moieties on the final nonwetting behavior. Influence of Si spike morphology to the final surface hydrophobicity is shown in Figure 9. The dependence of living cell adhesion on the surface morphology and hydrophobicity was also observed.
Quantum-mechanical perception of hydrophobicity at nanostructured surfaces

Hydrophobic effects comprise two distinguishable aspects: the transfer of a nonpolar substance from the gas phase into water, or hydrophobic hydration, and the association of nonpolar moieties in aqueous solution called hydrophobic interaction. The microscopic understanding of hydrophobic hydration relies, so far, almost solely on theoretical simulations since experimentally probing hydrophobicity at the atomic scale is very difficult, and quantitative studies are not yet available. Different computation methods are used for studying surfaces’ hydrophobicity since a single simulation method can hardly describe the high complexity of the interfacial systems. One of the important criteria to define the thickness of an interface is density which rapidly changes in the interface boundary. According to the Ohto et al., thickness of the interfacial water region depends on the functional used such as Becke–Lee–Yang–Parr, Perdew–Burke–Ernzerhof (PBE), and Revised Perdew–Burke–Ernzerhof generalized gradient approximation (GGA) functionals due to the predicted fraction of the interfacial water molecules. Hence, density functional theory (DFT) is one of the suitable methods that can be used for studying of wettability or wetting behavior, and recent progress relies on experimental studies using scanning probes in combination with theoretical calculations by DFT that provide a critical way to examine different structural models at the single-molecule level depending on the symmetry and chemical identity of the surface. Another important criterion is the orientation of molecules due to different chemical properties of surfaces. The molecules in the interface region prefer to be oriented, and the orientation fades with increasing distance from the surface. For this parameter, the most suitable computational method is molecular dynamics (MD). Therefore, this section provides recent progress in studying different surfaces composed of metals, metal oxides, sulfides, and other molecules and studying different surface roughness using DFT and MD computational methods.

Wettability of metal nanosurfaces acquired by DFT studies

The affinity of the different materials for water is primarily based on their electronic structure, and according to this interpretation, a hydrophilic material presents empty metal orbitals available to accept electrons from the water oxygen, whereas a hydrophobic material presents empty metal orbitals available to accept electrons from the water oxygen, whereas a hydrophobic material presents empty metal orbitals available to accept electrons from the water oxygen.
The density functional theory method can accurately describe the electronic polarization of a metal surface, and the interaction potential between the water and the metal surface relies on a proper choice of nonlocal correlation functionals. There are several studies that examine hydrophobic and hydrophilic characteristics of nanomaterial that are mentioned in Figure 10.

**Metal oxide and metal sulfide surface models**

The most-studied surfaces are TiO₂ and MoS₂ due to their various applications. Fatemi et al. provided a short review describing these materials with the DFT method, mostly oriented toward dissociation of water on the mentioned surfaces. With the TiO₂ surface, water dissociated on the defect sites into hydroxyl groups while wettability of water on the MoS₂ surface is more dependent on van der Waals interactions. Different studies also investigated stability of water on combined TiO₂ with different materials interfaces. Moreno et al. studied TiO₂-TiN since TiN is a widely used coating material with an ability to enhance the hardness, resistance to corrosion, and biocompatibility. Their results using DFT+U with PW91 functional show that when rutile TiO₂ (110) grows on TiN, the water is present in high coverage and dissociates only at very low PH₂O. Czelej et al. investigated doped TiO₂ with rare-earth metal Ce to increase hydrophobicity of hydrophilic TiO₂ since Azimi et al.’s experimental results showed that lanthanide's metal series possesses intrinsic hydrophobicity. However, Czelej et al.’s results obtained with DFT using PBE functional showed that the water contact angle does not change with Ce-doped TiO₂(110) surfaces regardless of Ce concentration and it is unlikely that the hydrophobicity of TiO₂(110) will be achieved through doping with Ce.

Beside wettability of TiO₂ surfaces, researchers also investigate the wettability of other metal oxide surfaces since metal oxides are commonly applied as electrode components for energy storage devices, substrate materials for optoelectronic devices, and catalysts. Zhu et al. used DFT with PBE functional and van der Waals correction to examine the anisotropic wettability of α-Al₂O₃ (11T0), (0001), and (1T02) surface which led to the conclusion that α-Al₂O₃ (1T02) is intrinsically hydrophobic with a water contact angle near 90°, while another three crystal faces are intrinsically hydrophilic with water contact angles < 65°.

Sulfides are also extensively studied group of metal surfaces since their natural floatability has been a controversial issue over the years. Zhao et al. examined the H₂O adsorption on sulfide surfaces (FeS₂, ZnS, PbS, Cu₂S, Sb₂S₃, and MoS₂) using DFT with PW91 functional to study the natural hydrophobicity. According to their results, FeS₂ and ZnS surfaces are hydrophilic, while PbS, Cu₂S, Sb₂S₃, and MoS₂ are hydrophobic. Besides, FeS₂ is also aerophilic since it can adsorb N₂ molecules. Long et al. confirmed these results through their investigation of water molecules on PbS and ZnS surfaces by DFT using PBE and PW91 functional. They suggested that the ZnS (110) surface exhibits a greater hydrophilic character than the PbS(100) surface. However, these simulations just took ideal sulfides as the study subject. The effect of sulfur produced in the oxidation process of FeS₂ on the hydrophobicity was investigated by Xi et al. with DFT GGA-PW91. Xi et al. showed that after the partial oxidation on the FeS₂ surface, the hydrophilicity of the FeS₂ surface was weakened overall and water molecules could not be spontaneously absorbed on a monolayer of the S-covered surface. Furthermore, the FeS₂ surface changed from hydrophilic to hydrophobic after complete oxidation of the pyrite surface. Deng et al. with the use of DFT-PW91 found that the In- and Ge-doped ZnS have different character and floatability from ideal ZnS. Although ideal ZnS, ZnS doped with In, Ge, and Fe are all hydrophilic, the Fe atom improves the hydrophilicity, while the In and the Ge atoms reduce the hydrophilicity of the (Zn, Fe)S surface.

**Rare-earth metal oxide surfaces models**

Recent experiments have identified robust intrinsic hydrophobicity of surfaces in rare-earth oxides (REOs), giving a prospect to multiple novel applications. Carchini et al. described wetting properties of CeO₂ and Nd₂O₃ in terms of geometric and electronic effect and compared them with common, highly wettable Al₂O₃ by DFT using PBE.

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**Figure 10.** Proposed model of the interaction of water at the interface with two prototypical oxides: (a) a-alumina and (b) rare-earth oxides by different studies. Reprinted with permission from Carchini et al. Copyright © 2016 American Chemical Society.
While Al₂O₃ exhibited perfect wetting by deposition of an ice layer on the Al₂O₃ surface, the adsorbed ice on REOs did not match the lattice parameter of materials, which led to partial dissociation of water, intrinsic nonwettability, most probably caused by geometric contribution (Figure 12). On the other hand, Carchini et al. also determined that REO’s surfaces with defects can react with water and generate persistent hydroxyl groups on the surface which can lead to appearance of perfect wetting. The CeO₂ surface was studied more in depth by Fronzi et al. by applying DFT-PBE on CeO₂ (111), (110), and (100) surfaces. The CeO₂ (111) surface was found to be the most hydrophobic with θ = 112.53° followed by (100) with θ = 93.91°. In contrast, the CeO₂ (110) surface was found the most hydrophilic with θ = 64.09°, and the contact angles increased for all three surfaces when O vacancy was present. Moreover, their findings imply that CeO₂ (100) surfaces formed in an aqueous environment (through sol–gel synthesis, for example) are likely to exhibit different surface properties from materials prepared using vacuum-based methods (e.g., pulsed laser deposition) since the O-terminated (100) surface was found to be unstable in the absence of full H₂O coverage, while in the absence of water, CeO₂ (100) surfaces are partially Ce terminated.

Zemla et al. employed DFT with the Hubbard U parameter correction (DFT+U) method with PBE functional to analyze the wettability of the Al₂O₃ surface doped with Eu, Nd, and Ce. The results show that Eu-, Nd-, and Ce-doped surfaces are hydrophobic, and higher values of contact angle can be correlated with roughness of surface

Figure 11. Computed adsorption models of the H₂O molecule on various sulphide surfaces with computationally determined distances in Å for investigation of wettability: (a) FeS₂, (b) ZnS, (c) PbS, (d) Cu₂S, (e) Sb₂S₃, and (f) MoS₂. Reprinted with permission from Zhao et al. Copyright © 2014 Elsevier.
structure and relatively long bond length between RE metal atoms and the oxygen forming a bridge with the ice-like water bilayer. Several studies have investigated the wettability of different surfaces; however, most of them examined the ideal surfaces, as displayed with sulfides. Therefore, computational DFT studies should also focus more on nonideal surfaces, which exhibit different hydrophilic/hydrophobic character.

Molecular dynamics simulations

The system size and timescale are quite limited when applying DFT, as only a few hundred atoms and picoseconds of measurement are affordable with regard to computational cost, thereby hampering the ability to obtain a full understanding of the liquid structure and dynamics. On the other hand, classical (MD) simulations have been a powerful tool to examine liquid structures and dynamics. MD feature the numerical solution of the classic equations of physical motion (Newton’s equations) of atoms and molecules and are used for predicting of the surface tensions of liquids and solid surfaces and contact angles of liquid nanodroplets since these terms cannot be easily measured experimentally.

Different dynamic models of hydrophobicity at nanotextured surfaces

The droplet in either the Wenzel state or the Cassie state depends on the height of the pillars and the pillar surface fraction. Therefore, a great number of studies use MD to study the mechanism of wettability, nanoflow, and interfacial properties of nanostructured surfaces with different nanopatterns such as hierarchical and nonhierarchical nanostructures or surfaces with nanopillars and minor bumps with different roughness.

Zheng et al. suggested by investigation of effects of nanoscale topography on nanoscale wettability with MD models the possibility of building a surrogate sinusoidal surface that exhibits very similar nanoscale wetting behavior as a surface having a natural roughness. Chen et al. studied the mechanism of how the nanostructure changes surface wettability on the molecular level placing 2856 water molecules on flat surfaces with different...
characteristic energies and on pillar surfaces with different pillar surface fractions. According to their results, the nanostructured surface is more hydrophobic than the flat surface and preferred to form the Cassie state, while the Wenzel model was not appropriate at nanoscale. The static contact angle would increase with the decrease of pillar surface fraction. Hydrophobic surfaces with nanoscale pillars were also investigated by Zhang et al.\textsuperscript{106} Using an atomistic MD simulation, they studied the drying transition of water confined between periodic square or circular pillars as the inter-pillar spacing was decreasing and the transition from a long-lived (metastable) Cassie–Baxter to the Wenzel state and vice versa. They found that the surface of water slowly reached the half height of the pillar with a significant up-and-down movement. Once the water surface reached the half height, it quickly penetrated down to the bottom (for the CB-to-WZ transition) or receded to the top of the pillar (for the WZ-to-CB transition). On the contrary, Kwon et al.\textsuperscript{106} investigated the static behavior of a water droplet on the surfaces with nonhierarchical and hierarchical roughness by using realistic all-atom MD simulations (Figure 13). A droplet on a surface with a hierarchical roughness tends to be in the Cassie–Baxter state, even when the droplet on the surface with a nonhierarchical roughness was in the Wenzel state.

**Elemental metal surfaces and alloys with nanotexture**

**Noble metal surfaces.** Molecular dynamics simulations also determine the wettability of different metal surfaces and wettability of the metal surface with different roughness. The most studied surfaces are noble metals such as Au, Ag, and Pt, since noble metals are most commonly used metals for probes or sensors\textsuperscript{110} and transparent electrodes for electronic devices.\textsuperscript{111} The change in surface wettability of the gold surface engraved with nanoscale (hemi)spherical cavities of various depths was studied by Zhang et al.\textsuperscript{112} using large-scale MD simulations. According to their results, with the increasing depth of the surface cavities, the water droplet varied from hydrophilic (73°) to hydrophobic (> 90°) and existed in various states, including the CB, WZ, and intermediate states, in which the cavities were partially filled with liquid. This was also in accordance with the experiment by Abdelsalam et al.\textsuperscript{113} On the other hand, Yang et al.\textsuperscript{114} studied wetting characteristics of a molten Ag-Cu-Au alloy on Cu substrates since Ag-Cu-Au is a promising alloy bonding wire for semiconductors. According to their results of MD wettability measurements of binary Ag-Cu and ternary Ag-Cu-Au droplet models on Cu(100), Cu(111), and Cu(110) substrates, ternary Ag-Cu-Au alloy with contact angle at equilibrium 25.2° with the largest tendency of solder spreading and greatest variation of dissolution degree has a higher solubility than that of binary Ag-Cu with contact angle 19.7°. Their computational results also illustrate that solid–liquid adhesion in W states is stronger than in the C wetting state. Chung et al.\textsuperscript{115} studied Ag nanocluster wettability on Cu-Ni alloys to overcome the oxidation problem of Cu-Ag core-shell particles for application to the electrodes of electronic devices. They used MD simulations for the (111) surface structure of Cu-Ni alloys and observed the compatibility between Ag and Cu-Ni alloys for the enhancement of Ag wettability by alloying Ni into Cu. Their results on the Ag wettability of Cu-Ni alloys show that the contact angles of Cu-Ni alloys are decreased with the increased Ni content in the alloys, which means the higher the Ni content of Cu-Ni alloys is, the better the compatibility between Ag and Cu-Ni alloy is.

Pt as another noble metal plays a fundamental role in aqueous electrochemistry where water often acts as solvent and reactant. MD simulations address the gap in knowledge of the large length scale correlations and emergent behavior of water on metal surfaces, even though such effects are likely to influence function in important ways.\textsuperscript{115} Limmer et al.,\textsuperscript{115} by applying MD study on structure and dynamics of liquid water in contact with metal surfaces Pt(100) and Pt(111), offered microscopic explanation and generalization of previous experimental observations that have inferred hydrophobicity of a platinum surface at low temperatures.\textsuperscript{116,117} Their results show that Pt(100) is more hydrophobic than the Pt(111) surface and that a hydrophobic surface formed from a passivated adlayer of water is accompanied by the existence of a liquid–vapor-like interface separating the adlayer from the bulk liquid. Wettability of metal surfaces is also investigated in the combination with different carbon nanomaterials. Among many two-dimensional nanomaterials, graphene has significant effects on metal substrates which include importance of graphene coating on the wetting behavior of substrates.\textsuperscript{119} The contact angle of water on graphene is presented to be ∼95–100°; however, the wetting behavior of the graphene is a complex subject and the notion that the graphene is hydrophobic may be debatable.\textsuperscript{75,120} Nguyen et al.\textsuperscript{119} conducted a series of MD simulations of water droplets on a bare copper substrate and graphene-coated copper substrates. They demonstrated that the graphene coating reduces the interaction strength between copper and water, and therefore, the study revealed the fact that hydrophobic surfaces can be obtained effectively via graphene coating, which reduces the solid–liquid interaction strength and changes the contact angle of the liquid on the solid substrate. However, in this study, the graphene layers used for coating were perfectly smooth, and therefore, the surface roughness also needs to be included.

**Carbon surfaces.** On the contrary, graphene may not only be used as the coating for metals but also metal surfaces may be used as substrates. Background underlaying metal substrates can also significantly affect the wettability of
graphene and graphene-water interactions and have considerable implications for graphene-based surface coatings. Yaghoubi et al.\textsuperscript{121} were interested in the reason of graphene-platinum interaction being weakest among the transition metals, and consequently, less affected graphene properties by the underlying platinum. They performed molecular dynamics simulations to investigate the wettability of water nanodroplet on striped patterned mono- and three-layer graphene supported underlying Pt (Figure 14). Their results indicated that the surface roughness of the supported substrates could lead to the CB or W states and that the wettability degree depends on the state. In the W state, the hydrogen bond lifetime and residence time at interface increases with significant increase in solid–liquid adhesion, while in the CB state, the adhesion decreases due to surface roughness.

Although the graphemic surface exhibits huge application potential, it cannot be applicable immediately due to the chemical inertness of graphitic network and hydrophobic nature of carbon surfaces. Hence, researchers tend to overcome the drawbacks of graphemic surfaces by their functionalization with oxygen-containing groups.\textsuperscript{122–124} Duch et al.\textsuperscript{122} used DFT calculations with PBE+D functional with Grimme empirical London dispersion term (PBE+D) to investigate the stability of oxygen plasma modified graphenic surfaces emphasizing wettability and electronic properties. Their results show that $\sim 6$ wt.% of surface oxygen (-OH, -CHO, and -COOH), led to dramatic changes in work function (increase by 1.15 eV) and the water contact angle (decrease by $74^\circ$).

Additional MD studies are interested in the wettability investigation of metals over carbon nanotubes since metallic films over carbon nanotubes exhibit extraordinary mechanical, optical, electronic, and catalytic properties.\textsuperscript{125} Kumar et al.\textsuperscript{111} studied the wetting and phase transition of gold onto a SWCNT using MD simulations and found that the gold depicts poor wettability into a SWCNT and that the interaction potential between gold and carbon atoms of SWCNT is responsible for wettability. At low interaction potential, gold depicts very poor wettability and evolves into a globular structure over the SWCNT. As interaction potential increases, wettability of gold enhances over the SWCNT. Zhou et al.\textsuperscript{126} investigated the mechanical properties of the Ni-coated or uncoated armchair SWCNT/magnesium matrix composites under axial tension using the MD simulation method. The results show that the tensile strength and Young’s modulus of the Ni-coated SWCNT/Mg composite are larger than those of the uncoated SWCNT/Mg composite and that the Ni-coated SWCNT can drastically increase the interfacial bonding between the SWCNT and the Mg matrix. This indicates that surface Ni coating of SWCNTs can provide an effective channel for load transfer of the SWCNT and Mg matrix because of the wettability improvement of the nanotube surface and Mg matrix.

**Metal sulfide surfaces.** Anvari et al.\textsuperscript{127} evaluated line tensions and contact angles of PbS(001) and ZnS(110) by MD simulations at 298 K. According to their results, the PbS surface with stronger hydrophobic character exhibited positive line tension, while ZnS exhibited strong interactions with water and showed negative line tension. Anvari et al.\textsuperscript{128} continued in computational studies of ZnS(110) hydrophilic character and modified the surface with n-butylthiol and i-butylthiol with different coverages.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure14.png}
\caption{Side and top views of Kumar et al.’s\textsuperscript{121} computational study of gold film wetting behavior over SWCNT with increasing time. Reprinted with permission from Yaghoubi and Foroutan. Copyright © 2018 American Chemical Society.}
\end{figure}
Their results indicate that with higher butylthiol coverage, the modified ZnS(110) surface becomes hydrophobic. Beyond 85% coverage, the calculated contact angles were much lower in the case of i-butylthiol which Anvari et al. explain is the result of stronger van der Waals interactions between H2O molecules and i-butylthiol due to the presence of two methyl groups in the tail group. The results suggest that simpler molecules such as butylthiol may substitute commercially used xanthanes as collectors in the flotation of sulfide minerals.127,129

Conclusions

Hydrophobicity at nanostructured surfaces is an important behavior of materials that plays a crucial role in many different fields of chemistry including material, colloidal science or simply in everyday life. Understanding of the process and development of novel materials with interesting hydrophobic or hydrophilic properties is essential for material applications in different industrial or commercial areas. Therefore, this review presented a current perception and utilization of hydrophobicity at nanostructured surfaces and development of novel materials with emphasis placed on this effect. Computational research is a rapidly expanding field in which attention is also directed toward hydrophobicity, mainly of materials where contact angle obstructs are measured, for example, when material is porous. It has shown that DFT studies of hydrophobicity mainly describe TiO2 and MS2 metal surfaces doped with various metals due to their different applications. Hydrophobicity DFT studies of rare-earth metal oxide surfaces are also increasing since REOs offer multiple novel applications. However, the results of these studies are obtained mostly on ideal surfaces and therefore may not present the realistic view which we think should be emphasized more in future DFT studies of hydrophobicity. Hydrophobicity at the nanostructured surface is an important scientific and technological field of research. It is an interdisciplinary subject involving chemistry, physics, and material sciences. Young, Wenzel, and Cassie–Baxter theories are used to describe wetting phenomena fundamentally. Here, we have attempted to identify phenomena associated with wetting firstly. We have emphasized that chemical composition, geometry, surface roughness, and anisotropy in surface structuring play an important role in the evaluation of hydrophobicity. Modification of surface hydrophobicity involves several procedures often used together.

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