REVIEW

Superhydrophobic surfaces for the reduction of bacterial adhesion

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As an important research area, the development of antibacterial materials has attracted extensive interest from researchers. Typical antibacterial materials involve the use of biocides and antibacterial metallic ions, such as Ag^+, as well as killing by highly reactive species, such as hydroxyl radical, hydrogen peroxide and superoxide produced by the photocatalysis of TiO_2. However, the intensive usage of biocides has a growing concern in the increase of bacterial resistance and cross-resistance to antibiotics and antibacterial Ag^+ depending on its dissolution property may have potential implications on human health and environment. Currently TiO_2 is mainly activated with UVA light and research on visible light photocatalysis is still under development. Recently, a new scheme using superhydrophobicity has raised more attention and interests especially for its ability in reducing bacterial adhesion. This paper provides a detailed review on the basics, recent developments, existing challenges and future perspectives of superhydrophobic surfaces especially in reducing bacterial adhesion.

1 Introduction

The adhesion and proliferation of bacteria on abiotic surfaces and the subsequent biofilm formation pose challenges in both healthcare and industrial applications. The design of anti-

bacterial materials has been a long-standing effort and a number of strategies have been developed to limit bacterial colonization on material surfaces. The first approach, as the oldest method for antibacterial surface design, focuses on leaching biocides (for example cytotoxic compounds from a surface) and inducing the death of both the adhered bacteria and nearby bacteria.[1] However, while the biocides are widely used in everyday life to limit potential sources of infection, there is a growing concern that an increasing use of biocides can result in higher bacterial resistance and the cross-

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resistance to clinically important antibiotics.[2] It has thus been suggested that biocides should be much more prudently used.[3–5] Antibacterial metals, such as Ag,[6] Cu[7] and Mo,[8] with Ag being the oldest and most popular one, are also used as a type of antibacterial agent to induce the death of adhered bacteria by their metallic ions. The antibacterial effect of Ag is mainly based on Ag^+ ions and therefore dependent on the dissolution rate of Ag.[6] When Ag is dissolved completely from the surface, its antibacterial effect will be gone. Besides, there are also growing concerns on its bacterial resistance and its potential implications for human health and the environment.[9,10]

More recently, strategies which do not involve the use of biocides and antibacterial metallic ions have also been developed. One approach uses photocatalytic materials such as TiO_2 to produce highly reactive species such as hydroxyl radical, hydrogen peroxide and superoxide to kill bacteria.[11] This method has been successful in killing *Escherichia coli* cells and some other types of bacteria.[12,13] However, TiO_2 is mainly active with UVA light and research is being carried out in activating TiO_2 using visible light.[14,15]

Developing antibacterial materials based on superhydrophobicity is a new strategy that has been recently developed. Traditionally, only the materials that can induce the death of bacteria have been referred to as antibacterial materials. It is more and more acceptable to include superhydrophobic surfaces in this category even though they reduce bacterial adhesion rather than killing them directly.[16–18] Superhydrophobicity can reduce the adhesion force between bacteria and a solid surface to enable the easy removal of bacteria before a thick biofilm is formed on the surface.[19] This paper provides a detailed review on the basics, recent developments, existing challenges and future perspectives of superhydrophobic surfaces especially in reducing bacterial

Fig. 1 The number of scientific publications with ''superhydrophobic'', ''super hydrophobic'', ''superhydrophobicity'' or ''super hydrophobicity'' in their titles from the ISI Web of Knowledge.

adhesion for antibacterial applications. In the following sections, the basics of superhydrophobic surfaces and wetting are firstly explained, followed by a summary of typical materials properties that affect bacterial adhesion on abiotic surface to provide an overview on the material-bacteria interaction. The fourth section highlights research on superhydrophobic surfaces that have reduced the adhesion of a variety of bacteria. Finally the challenges and future trends in applying superhydrophobic surfaces for the reduction of bacterial adhesion are discussed.

2 Superhydrophobic surfaces

The superhydrophobic surface is inspired by the Lotus leaf in nature, where a water contact angle of over 150° is observed.[20] It was suggested in 1997 that the Lotus leaf has a microscale surface topography that comprises convex microstructures (papillose epidermal cells) immersed in a dense layer of epicuticular waxes.[21] In 2002, it was further revealed that the Lotus leaf has a hierarchical micro/nanostructure.[22] Since then it has been commonly accepted that the superhydrophobic characteristic of the Lotus leaf is due to its hierarchical micro/nanostructures and the hydrophobic wax on top of the surface. Generally, water forms droplets on a Lotus leaf and rolls off easily when it is tilted. Research on superhydrophobic surfaces has attracted a significant amount of interest and its rapid progress is clearly shown in the fast growth of scientific publications. Fig. 1 shows the results of a search on the ISI Web of Knowledge using "superhydrophobic", "super hydrophobic", "superhydrophobicity" or "super hydrophobicity" in the titles of the publications.

2.1 Wetting phenomena

2.1.1 Wetting models. Wetting reflects how a liquid behaves on a solid surface. Young's equation is typically used to describe wetting on an ideal smooth surface. By assuming the solid surface is smooth, rigid, chemically homogeneous, insoluble and non-reactive, the contact angle (θ, the angle between γ_{sl} and γ_{lv}, in Fig. 2a) can be defined by Young's

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and thin film synthesis include sol–gel, supercritical carbon dioxide assisted synthesis and pyrolysis methods aiming to multifunctional materials with self-cleaning, antibacterial, photoactive, bioactive and catalytic properties. Professor Levänen is currently author of 150 publications from which 45 are peer-reviewed.

Fig. 2 Illustration of a liquid droplet on an ideal smooth surface in (a), on a rough surface in a Wenzel regime in (b) and on a rough surface in a Cassie–Baxter regime in (c). Reprinted by kind permission from Macmillan Publishers Ltd: *NPG Asia Materials*, A. Nakajima, Design of hydrophobic surfaces for liquid droplet control, 2011, **3**, 49–56, Copyright (2011).

equation[23,24] as follows:

$$\cos\theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \qquad (1)$$

where θ is Young's contact angle, γ is the surface tension defined as the force per unit length of the interface and s, l and v represent the solid, liquid and vapour respectively. Therefore, γ_{sv} is the surface tension between the solid phase and the vapour phase, γ_{sl} between the solid phase and the liquid phase, and γ_{lv} between the liquid phase and the vapour phase (see Fig. 2a). γ is also often referred to as the surface energy or surface free energy in literature, which is the amount of energy applied to break chemical bonds. Molecules that do not form chemical bonds on the surface tend to have a higher energy, *i.e.* surface free energy, than those that form chemical bonds.[25] The surface free energy is measured in unit of Joules per square meter ($J\ m^{-2}$), which is equivalent to a surface tension measured in Newtons per meter ($N\ m^{-1}$). Though thermodynamically the surface tension and surface free energy are different, they are numerically equivalent and often referred to as the same thing in literature.[20] However, in practice, in dealing with liquids, the surface tension is usually used while the surface free energy is a more general term for solids.

In real situations, solid surfaces are usually rough and chemically heterogeneous. Wetting on a rough surface often takes place in two different regimes, as shown in Fig. 2b and 2c. In Fig. 2b, the liquid has completely penetrated into the roughness grooves and it is called homogeneous wetting. In Fig. 2c, there is air entrapped in the roughness grooves underneath the liquid and it is called heterogeneous wetting.[16] On a superhydrophobic surface, water usually has heterogeneous wetting where air is entrapped between the water droplets and the surface.

Homogeneous wetting can be described by Wenzel equation[26] below,

$$\cos\theta_A = r\cos\theta_Y \qquad (2)$$

where θ_A is the apparent contact angle, r is the roughness parameter (or roughness ratio) defined as the ratio of the actual contacting area of a rough surface to the geometric projected area, and θ_Y is Young's contact angle on a flat surface. The apparent contact angle was introduced for

wetting on rough surfaces because the actual contact angle is often inaccessible. The apparent contact angle is the angle between the tangent to the liquid-air interface and the line that represents the normal solid–liquid interface.[27] The difference between the two contact angles could be large. The Wenzel equation also states that both hydrophilicity and hydrophobicity are enhanced by roughness, that is a rough hydrophilic surface ($\theta_Y < 90°$) becomes more hydrophilic, and a rough hydrophobic surface ($\theta_Y > 90°$) more hydrophobic than a smooth surface with the same chemical composition.[28]

On the other hand, heterogeneous wetting can be described by the Cassie–Baxter equation[29] below,

$$\cos\theta_A = f_1\cos\theta_1 - f_2 \qquad (3)$$

where θ_A is the apparent contact angle, f_1 is the fraction of solid material in contact with liquid, θ_1 the contact angle of the pure solid material and f_2 the fraction of air in contact with the liquid ($f_1 + f_2 = 1$).

It is also suggested that heterogeneous regime on a superhydrophobic surface is thermodynamically metastable, while homogenous regime is stable.[30] The metastability or the regime transition can be demonstrated in several ways. For instance, by applying a small pressure on the metastable Cassie–Baxter droplet, the droplet can slip to the stable Wenzel regime. Similarly, a Cassie–Baxter droplet can recede into a Wenzel droplet by allowing a small amount of the liquid to evaporate. The state of the droplet also depends on the amount of liquid and the means of depositing the liquid on the surface. For instance, when the liquid is delivered in the form of a mist, it wets the surface instantly as a Wenzel droplet.[16]

2.1.2 Contact angle, contact angle hysteresis, roll-off angle and sliding angle. When the contact angle (θ) is $0°$, the droplet spreads completely on the solid surface and this is referred to as complete wetting. On the contrary, when θ is $180°$ the droplet stands on the surface and it is named as non-wetting. The above two cases are the two extremes. When water is used as the liquid, the surface is hydrophilic when the contact angle is less than $90°$. Superhydrophilic surfaces are those with contact angles for water less than $5°$.[31] On the other hand, a surface is hydrophobic when the contact angle for water is above $90°$ and superhydrophobic when it is more than $150°$.

Contact angle hysteresis means that two different contact angles exist along the contact line of a droplet, as shown in Fig. 3, where the advancing angle θ_a at the front of the drop is larger than the receding angle θ_r at the rear of the drop.[32] The contact angle hysteresis is therefore defined as the difference between the advancing and receding angles:

$$H = \theta_a - \theta_r \qquad (4)$$

Contact angle hysteresis is an important parameter in understanding drop motion on a surface. In practice, hysteresis is caused by surface roughness, contamination, chemical heterogeneity, drop size, molecular orientation and deformation, and liquid molecular transport.
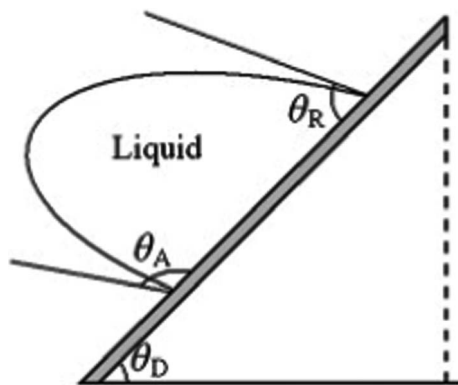
Fig. 3 Illustration of a droplet moving along an inclined surface with advancing angle θ_a and receding angle θ_r. Reprinted from *Advances in Colloid and Interface Science*, 2011, **169**, Y. Y. Yan, N. Gao and W. Barthlott, Mimicking natural superhydrophobic surfaces and grasping the wetting process: A review on recent progress in preparing superhydrophobic surfaces, pages 80–105, Copyright (2011), with kind permission from Elsevier.

In addition to the hysteresis, the roll-off angle or tilt angle is also defined as the angle at which the droplet starts to roll off from an inclined surface.[30] Surfaces with low roll-off angle or tilt angle tend to have low contact angle hysteresis.[33] In most cases, water has very low roll-off angles of a few degrees on superhydrophobic surfaces. However, sticky superhydrophobic surfaces with high contact angle hysteresis have also been reported.[34] The critical angle at which the droplet with a certain weight begins to slide down the inclined surface is defined as the sliding angle.[35] Typically rolling only occurs on a superhydrophobic surface, while sliding happens on other surfaces if the droplet could move.

2.1.3 Surface free energy. Various approaches have been used to determine the surface free energy of solid materials. In the Owens and Wendt geometric mean approach, the surface free energy is divided into two components: dispersive and polar.[36] The resulting equation when combined with Young's equation is:

$$\gamma_L (1 + \cos\theta) = 2 \left[(\gamma_L^P \gamma_s^P)^{1/2} + (\gamma_L^d \gamma_s^d)^{1/2} \right] \quad (5)$$

where θ is the contact angle, γ_L is the liquid surface tension and γ_s is the solid surface tension or surface free energy. The additions of d and p in the superscripts refer to the dispersive and polar components of each. The total surface free energy is merely the sum of its two components. To obtain the γ_s^d and γ_s^P of a solid, the contact angles of at least two liquids with known surface tension components (γ_L, γ_L^P, γ_L^d) on the solid must be determined.[37] On the other hand, if the liquid has only the polar component in its surface tension, and the solid only has the dispersive component in its surface tension, wetting will not happen, and *vice versa*.

The other well accepted approach is the acid–base theory (LW/AB theory) proposed by van Oss *et al.*[38] In their approach, the surface free energy is decomposed into γ^{LW} and γ^{AB}:

$$\gamma = \gamma^{LW} + \gamma^{AB}, \text{ with } \gamma^{AB} = 2(\gamma^+\gamma^-)^{1/2} \quad (6)$$

LW stands for Lifshitz–van der Waals interactions, which include the London dispersion, Keesom dipole–dipole and Debye induction. AB represents Lewis acid–base interactions. γ^+ and γ^- are the Lewis acid (electron-acceptor) and Lewis base (electron-donor) parameters of the surface free energy, respectively. The larger γ^+ is, the stronger ability it has to accept electrons. On the other hand, the larger γ^- is, the stronger ability it has to provide electrons. In order to determine the three unknowns (γ^{LW}, γ^+, γ^-), three test liquids with known surface energy parameters are required.

Surface energy is an intrinsic property of materials. Low surface energy molecules include primarily methylated and fluorinated carbons, with surface energy decreasing in the following manner: $-CH_2- > -CH_3 > -CF_2- > -CF_2H > -CF_3$. The lowest surface energy of any readily available solid is 6.7 mN m^{-1} based on the hexagonal closed alignment of $-CF_3$ groups on the surface, which gives a water contact angle of 119° on a smooth surface.[39] Therefore, in order to achieve a contact angle for water of over 119°, a rougher surface is required, according to the Wenzel equation.

2.1.4 Free energy of interaction. Instead of using the contact angle, another way of characterizing surface hydrophobicity and hydrophilicity is to calculate the free energy of interaction between a surface (i) and water (w) (ΔG_{iwi}) using the surface energy components. The equation is as follows:[40]

$$\Delta G_{iwi} = -2 \left(\sqrt{\gamma_i^{LW}} - \sqrt{\gamma_w^{LW}} \right)^2 - $$
$$4 \left(\sqrt{\gamma_i^+ \gamma_i^-} + \sqrt{\gamma_w^+ \gamma_w^-} - \sqrt{\gamma_i^+ \gamma_w^-} - \sqrt{\gamma_w^+ \gamma_i^-} \right) \quad (7)$$

By definition, hydrophobic surfaces are those with $\Delta G_{iwi} < 0$, whereas hydrophilic surfaces are those with $\Delta G_{iwi} > 0$. Superhydrophobic surfaces are those with $\Delta G_{iwi} < -84$.

2.2 Lotus effect: self-cleaning

The Lotus effect was introduced in 1997 to explain the self-cleaning property of the Lotus leaf.[41] For centuries the Lotus has been the symbol of cleanliness in Asian culture. Due to the low surface energy of the waxes and the surface topography shown in Fig. 4a, the Lotus leaf has a very high water contact angle of 170° and a very low roll-off angle of a few degrees. On such a surface, air is entrapped in most of the surface area, hence significantly reducing the contact area between water and the leaf surface as well as that between the dirt particles and the leaf surface. This considerably reduces the adhesion force of water as well as the dirt particles to the leaf surface. Therefore the adhesion of dirt particles to the leaf surface is much weaker than that to the water droplet. When the water droplet rolls off from the leaf surface, dirt particles are taken away, as illustrated in Fig. 4b and Fig. 5a. This phenomenon has been referred to as the Lotus effect. On the contrary, on a titled smooth surface the water droplet tends to slide off the surface. It passes through the dirt particles leaving the particles on the surface (illustrated in Fig. 5b).

To be more precise, a superhydrophobic surface is easy-to-clean rather than self-clean. Zhang *et al.*[42] tested a super-hydrophobic surface in a paper machine and revealed that the
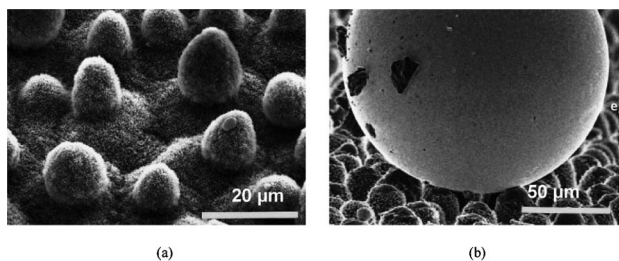
Fig. 4 A scanning electron microscopy image of a Lotus leaf (*Nelumbo nucifera*) in (a) and an illustration of the reduced contact area of a mercury droplet on the leaf surface of a *Colocasia esculenta* and the contaminating particles adhering to the mercury droplet in (b). Reprinted from W. Barthlott and C. Neinhuis, Purity of the sacred lotus, or escape from contamination in biological surfaces, *Planta* 1997, **202**, 1–8, Copyright (1997), with kind permission from Springer Science and Business Media.

superhydrophobic surface was not self-cleaning (being clean by itself) but covered by contaminants from the paper machine environment. However, the contaminants could be easily cleaned by washing with pressure water due to the low adhesion force of the contaminants to the surface.

2.3 Other functionalities

In addition to the easy-to-clean property, superhydrophobic surfaces have been found to be able to reduce bacterial adhesion and have an easy removal capability of the bacterial cells slowing down the thick biofilm formation processes. Superhydrophobic surfaces are also believed to have other functionalities such as water repellence, broadband anti-reflection,[43,44] anti-icing,[45–47] drag-reduction in fluid flow,[48,49] non-adhesive property[50] and wetting control.[51,52]

2.4 General processing schemes

A number of processes for generating superhydrophobic surfaces have been extensively reported in the last two decades. It has been commonly accepted that low surface

Fig. 5 Illustration of a water droplet rolling off a rough surface in (a) and sliding on a flat surface in (b). Reprinted from W. Barthlott and C. Neinhuis, Purity of the sacred lotus, or escape from contamination in biological surfaces, *Planta* 1997, **202**, 1–8, Copyright (1997), with kind permission from Springer Science and Business Media.

energy and surface roughness are the two dominant factors in the processes, which have been in general separated into two approaches.[22,53] The first approach is to roughen a hydrophobic surface typically consisting of a polymer material with low surface energy, *e.g.* with methylated and fluorinated carbons groups. The other one is to coat low surface energy molecules such as fluoroalkylsilane on a rough surface of any type of material like ceramics or metals. The former is typically a one-step process and the latter a two-step process. However, some superhydrophobic surfaces have also been processed without deposition of low surface energy molecules on hydrophilic materials.[54–57]

Surface roughness can vary significantly, depending on the processing methods and processing parameters. A numbers of methods can be used to roughen a surface. Also a wide range of surface roughness (either random or tailored) can have heterogeneous wetting in the Cassie–Baxter state, resulting in a superhydrophobic property. Specific methods and routes to produce superhydrophobic surfaces are considered outside the scope of this review but details are available in many other publications.[20,51,58–63]

2.5 Typical characterization techniques

The most typical means for superhydrophobicity characterization is to measure the contact angle by a sessile droplet method.[64,65] A microliter syringe is used to release a water droplet and an optical system is connected to a computer for data analysis. Typically, 5 droplets are put on different positions on the surface and the average is accepted as the final value. Advancing, receding, sliding, and roll-off angles are obtained using the same system, if the sample holder platform can be tilted while the data is recorded. The sessile droplet method is relatively simple. However the results are dependent on the drop profile, the substrate baseline, contrast, lighting and focusing, and it becomes more complicated if the substrate is non-reflective and macroscopically rough.[66]

Recently, a new method has been developed to characterize superhydrophobicity based on the ability of water droplets bouncing on the surface, *i.e.* the number of water bounces.[67] It was found that water bouncing only occurred on the surfaces with a water contact angle of over 151°. The authors therefore concluded that a surface capable of achieving one or more bounces could be judged to be superhydrophobic (Fig. 6a). They also found that the number of bounces increased linearly with the water contact angle for surfaces with similar microstructures (Fig. 6b), *i.e.* a surface which supported 5 bounces was more superhydrophobic than one which supported 3 bounces. They suggested that this new technique provided a universal indication of superhydrophobicity and was able to rule out the disparity in measuring the static water contact angle.[67]

Superhydrophobicity is typically characterized in air, and is generally not applicable for submerged systems where the liquid volume is practically infinite. However, underwater superhydrophobicity is relevant in antibacterial applications, when a material surface is immersed in water where bacteria are suspended. One criterion suggested for underwater superhydrophobicity characterization is the area fraction of the
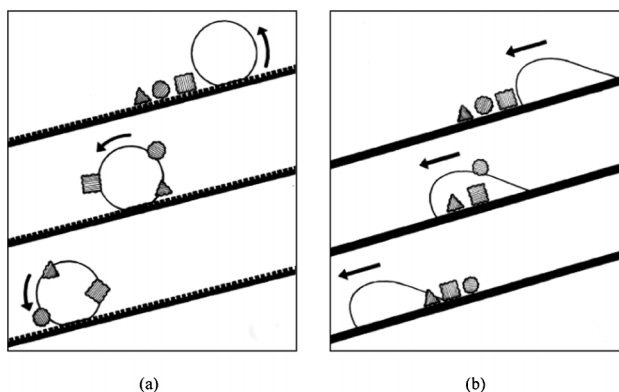
(a)

(b)

Fig. 6 Series of photographs of an 8 ml methylene blue colored water droplet dropped from a height of 20 mm and bounced on substrates with a range of water contact angles in (a), and the number of bounces on surfaces with a range of hydrophobicity in (b). Reprinted from C. R. Crick and I. P. Parkin, Water droplet bouncing – a definition for superhydrophobic surfaces, *Chemical Communications*, 2011, **47**, 12059–12061, Copyright (2011), with kind permission from Royal Society of Chemistry.

solid that is wet at equilibrium (Φ_e). Thus the goal of designing an underwater superhydrophobic surface has been to make the Φ_e as small as possible. In principle, underwater superhydrophobicity is achievable with a sufficiently high roughness ratio.[68]

2.6 Long term durability

Despite the extensive study of superhydrophobic surfaces, challenges still remain in applying them in real applications. As stated, superhydrophobic surfaces require a micro/nano surface roughness and a low surface energy, thus they generally suffer from weak durability due to the mechanically fragile micro/nano structure on the surface and the fast

degradation of surface chemistry. Robust superhydrophobic surfaces are generally unattainable at the required micro/nanoscales.[69] Any loss of the micro/nano topographical structures on the surfaces will lead to a reduction of its superhydrophobicity. The degradation of the low surface energy layer may lead to the loss of superhydrophobicity even when the surface topographical structure is undamaged. The degradation could be caused by surface contamination[63] and/or reactions of the layer with chemicals in the environment.[70,71]

Although plenty of studies have been carried out developing processes to create superhydrophobic surfaces, research on the durability aspect of superhydrophobic surface only started

a few years ago.[72] Several concepts to improve the mechanical durability of superhydrophobic surfaces are suggested, for example, by using hierarchical roughness in which robust microscale bumps can provide protection to the more fragile nanoscale roughness,[73,74] using composite materials with a hydrophobic polymer in the matrix,[75–77] and incorporating self-healing[78,79] and photocatalytic functions in superhydrophobic surfaces.[72] The uses of hierarchical roughness and composite materials have been currently considered as the most mature concept and other concepts are still in early development stages. It has also been found that, although the hierarchical roughness covered with a low surface energy layer has attracted a lot of attention, the wear out of the low surface energy layer and damage of the nanoscale roughness can result in an increase in the contact angle hysteresis and loss of superhydrophobicity.[73,74] Incorporating various nanoparticles in the hydrophobic polymer matrix in composite materials has been demonstrated as a reasonable approach to improve durability.[75–77] Despite the great efforts made so far, it is still challenging to obtain mechanically robust and chemically stable and durable superhydrophobic surfaces for demanding applications, and certainly much more effort and breakthrough solutions are required. For many applications where wear resistance is not essential, superhydrophobic surfaces can still be applied to achieve a good performance. For example superhydrophobic surfaces can be applied on the ceilings and walls of hospital buildings to reduce bacterial adhesion. Therefore it is important to understand the durability requirements in targeted applications in order to apply a proper processing method in preparing a suitable superhydrophobic structure.

3 Effect of material properties on bacterial adhesion

Although this review focuses on the reduction of bacterial adhesion *via* superhydrophobicity, it is important to explain how bacteria interact with materials and how material properties in general affect bacterial adhesion. This section thus identifies the materials properties and summarizes their effects on bacterial adhesion. It is not intended to provide concrete conclusions on the exact influence of a material property on bacterial adhesion, since contradictory results have been observed depending on the particular experimental conditions applied in different studies. Joint influences due to a number of material properties are often seen.

3.1 Bacterial adhesion in general

In general, bacteria are structurally and chemically complex and dynamic to environmental changes.[80] They can be classified by their shape or as Gram positive or Gram negative, which refers to a staining procedure, as shown in Fig. 7. For example *Staphylococcus epidermidis* is a spherical coccus and Gram positive, and *Escherichia coli* is a cylindrical bacillus and Gram negative.[81] The composition of the cell wall of Gram positive and Gram negative bacteria differs considerably.[80]

Fig. 7 Illustration of bacterial classification. Reprinted with permission from J. A. Lichter, K. J. V. Vliet and M. F. Rubner, *Design of Anti-bacterial Surfaces and Interfaces: Polyelectrolyte Multilayers as a Multifunctional Platform*, *Macromolecules*, 2009, **42**, 8573, Copyright (2009) American Chemical Society.

Classically, bacterial cells have been treated as inert particles and the bacterial adhesion to a flat surface have been widely described by the DLVO (Derjaguin, Landau, Verwey, Overbeek) theory in which particle adhesion is governed by van der Waals interactions (generally attractive) and repulsive interactions from the electrical double layer of the cell and the surface.[82] Bacterial adhesion is generally described by two stages resulting in mature biofilm formation, as illustrated in Fig. 8. Stage I is the initial interaction which is rapid and reversible between the bacterial cell surfaces and the material surfaces, while stage II involves specific and non-specific interactions between proteins on the bacterial surface structures (fimbriae or pilli) and binding molecules on the material surface. Stage II is slowly reversible and often termed as irreversible.[81] However, real cell-material interactions are far more complex as they involve highly dynamic cells, the environment with many variables such as temperature, pH, *etc.*, and material surfaces influenced by many different properties. This paper will focus on the effect of material properties on the bacterial adhesion.

3.2 Effect of surface charge

Surface charge is typically originated from atom substitution in a crystal lattice, lattice defects, broken bonds and the ionization of surface groups. The surface charge affects the distribution of ions in the surrounding interfacial region, resulting in an increased concentration of counter ions (ions of opposite charge to that of the particle) close to the surface. Thus an electrical double layer exists around each particle, and the Z potential is typically measured to indicate the thickness of the electrical double layer.[83]

The bacterial cell surface charge originates from the dissociation or protonation of carboxyl, phosphate and amino groups.[80] Under most physiological conditions, a bacterial cell

Fig. 8 Illustration of the two stages of bacterial adhesion. Reprinted with permission from J. A. Lichter, K. J. V. Vliet and M. F. Rubner, Design of Anti-bacterial Surfaces and Interfaces: Polyelectrolyte Multilayers as a Multifunctional Platform, *Macromolecules*, 2009, **42**, 8573, Copyright (2009) American Chemical Society.

surface carries a negative charge, with a few exceptions.[80,84] Therefore, the bacterial adhesion on negatively charged surfaces is generally reduced as bacteria experience an electric double layer repulsion when approaching the surface. On the contrary, bacterial adhesion tends to increase on positively charged surfaces.[85] However, Gottenbos et al.[86] found that positive surface charge could also impede bacterial growth, despite the initially promoted adhesion.

3.3 Effect of surface free energy

Bacterial adhesion on surfaces with different surface free energies has been widely studied and it has been proved that the surface free energy can significantly influence bacterial adhesion. A relationship between bacterial adhesion and the surface free energy was reported and a surface free energy between 23 and 30 mN m^{-1} was related to the lowest bacterial adhesion.[87] This is consistent with other reported results. For example, a minimum *Escherichia coli* adhesion was reported for the surface free energy range between 21 and 29 mN m^{-1}.[88] A minimum bioadhesive range and a highest detachment rate of marine biofilms was shown to exist for a surface free energy between 20 and 25 mN m^{-1}.[89] A tailoring of a total surface free energy between 20 and 27 mN m^{-1} and its LW component between 20 and 24 mN m^{-1} reduced the initial adhesion of *Pseudomonas aeruginosa* AK1 to inert surfaces.[90]

It is also reported that bacteria spreading was dependant on the polar component of the surface free energy (γ^{AB}). The spreading was low when the polar component was less than 5 mN m^{-1}, while high spreading occurred when the polar component was greater than 15 mN m^{-1}.[40] The Lewis acid (electron-acceptor, γ^+) and Lewis base (electron-donor, γ^-) parameters of surface energy have also been reported to have

influence on the growth and attachment of osteoblasts as surfaces with more electron acceptor sites encouraged osteoblastic differentiation.[40]

3.4 Effect of wettability

A lot of research has also focused on investigating the influence of surface hydrophobicity or hydrophilicity, in another word, the wettability on bacterial adhesion.[91–96] Arima and Iwata[91] found that bacteria effectively adhered onto polymer surfaces with water contact angles of 40–70°. Also, Lee et al.[92] reported that bacteria adhered, spread and grew more on a polyethylene surface with moderate hydrophilicity, with a maximum adhesion of bacteria at a water contact angle of about 57°. Both studies showed a good relationship between wettability and bacterial adhesion. Studies also showed that the hydrophilic surface attracted bacteria like *Staphylococcus aureus* and *Escherichia coli*,[93] whereas hydrophobic surface attracted *Pseudoxanthomonas taiwanensis* and *Staphylococcus epidermidis* and reduced the adherence of bacteria including *Deinococcus geothermalis* and *Meiothermus Silvanus*,[94] *Staphylococcus aureus*,[95] and *Streptococcus mutans*.[96]

Surface charge, surface free energy and surface wettability are related and often have joint influence on bacterial adhesion. Besides, they all depend on the surface chemical composition whose effect on bacterial adhesion is typically studied through surface wettability, free energy and charge of the material.

3.5 Effect of surface topography

It was found that irregularities in polymeric surfaces promoted bacterial adhesion and biofilm formation, whereas ultra-

Table 1 Summary of the bacterial adhesion experimental details and the main findings

Bacterium tested	Material and processing of the superhydrophobic surface	Test period	Main findings on the superhydrophobic surface	Ref.
Staphylococcus aureus (spherical shape, Gram positive)	Based on TiO$_2$ nanotubes processed by electrochemical oxidation and finally treated with silane	2 h and 4 h	Less adhesion than on hydrophobic and hydrophilic surfaces, scattered distribution, adhesion increased with time	101
	Based on fluorinated silica colloids	1.5 h	Reduced adhesion compared with reference	102
	Based on a silicone elastomer prepared by aerosol assisted chemical vapour deposition	1 h	Reduced adhesion compared with an uncoated glass and a dip-coated elastomer hydrophobic glass	103
	Superhydrophobic poly(L-lactic acid) surface	24 h	*No reduced bacterial adhesion*	106
	Laser ablated superhydrophobic Ti surface	18 h	*No reduced bacterial adhesion and bacterial colonization happened*	105
Pseudomonas aeruginosa (rod shape, Gram negative)	Based on fluorinated silica colloids	1.5 h	Reduced adhesion compared with reference	102
	Laser ablated superhydrophobic Ti surface	18 h	Nearly no bacterial adhesion	105
	Superhydrophobic poly(L-lactic acid) surface	24 h	*No reduced bacterial adhesion and biofilm formation happened*	106
Escherichia coli (rod shape, Gram negative)	polystyrene (PS), polycarbonate (PC) and polyethylene (PE) surfaces induced by shrink	NA	2% of bacteria adhered, < 0.1% of bacteria remained after rinsing	104
	Based on a silicone elastomer prepared by aerosol assisted chemical vapour deposition	1 h	Reduced adhesion compared with an uncoated and a dip-coated elastomer hydrophobic glass	103

smooth surfaces did not favour bacterial adhesion and biofilm formation.[97] This was explained by the fact that a rough surface processes a greater surface area with the depressions providing more favourable sites for bacterial colonization. By using natural surfaces the effect of surface topography on biofilm formation and subsequently their fouling in sea water was studied. One example of natural surfaces is the shell of the blue mussel *Mytilus galloprovincialis* which has a homogenous ripple-like microtextured surface (1–2 μm). It was reported with microtopography that the shell of *M. galloprovincialis* was fouled by significantly fewer species and had a significantly less total fouling cover than the smooth reference surfaces over a 12 week period in sea water.[98] An attachment point theory was later studied to explain the effect of surface topography on bacterial adhesion, the subsequent biofilm formation and fouling. Theoretically, the cell has the highest number of attachment points when it fits within the depressions in the microtextures, while 2 attachment points are the lowest when the cell is slightly larger than the microtexture wavelength.[99] In general, the surfaces with a higher number of attachment points will attract more cell attachment. However, the influence of the surface topography addressed here is not the same on superhydrophobic surfaces with Cassie–Baxter wetting schemes. The application of using superhydrophobic surfaces to reduce bacterial adhesion is reviewed in the next section.

3.6 Effect of other material properties

Apart from the above mentioned material properties, the elastic modulus and surface coating thickness were also reported to affect bacterial adhesion. Brady and Singer[100] found that the relative bioadhesion of pseudobarnacles on

various surfaces was related to $(\gamma E)^{1/2}$, where γ is the surface energy and E is the elastic modulus or Young's modulus. They also suggested that bacterial adhesion decreased when the coating thickness was increased to 100 μm. A coating thickness of more than 100 μm did not exhibit any major decrease in the adhesion.

4 Recent developments in applying superhydrophobic surfaces to reduce bacterial adhesion

Bacterial adhesion on hydrophobic surfaces has been extensively studied and it has been recently extended to superhydrophobic surfaces. The feasibility of using superhydrophobic surfaces to reduce bacterial adhesion has been investigated by a number of researchers.[101–118] This section reviews the superhydrophobic surfaces that have been shown to reduce bacterial adhesion and the mechanisms of how bacterial cells interact with superhydrophobic surfaces, evaluating the current development in applying superhydrophobic surfaces for the reduction of bacterial adhesion.

4.1 Superhydrophobic surfaces to reduce bacterial adhesion

Table 1 summarizes the experimental details and the main findings of the superhydrophobic surfaces that have shown the ability to reduce bacterial adhesion with a couple of exceptions.

Tang *et al.*[101] observed the adhesion of *Staphylococcus aureus* on surfaces with different wettabilities. The SEM images of the adhesion of *Staphylococcus aureus* on different surfaces after 2

Fig. 9 SEM images of *Staphylococcus aureus* adhesion after 2 h and 4 h on hydrophilic, hydrophobic and superhydrophobic surfaces with contact angles marked in the parentheses. Reprinted with permission from P. Tang, W. Zhang, Y. Wang, B. Zhang, H. Wang, C. Lin and L. Zhang, Effect of superhydrophobic surface of titanium on *Staphyococcus aureus* adhesion, *Journal of Nanomaterials*, 2011, article ID 178921.

h and 4 h are shown in Fig. 9. After 2 h, there were *Staphylococcus aureus* on their TiO$_2$ nanotube based super-hydrophobic surface with a water contact angle of 156° compared with those on the hydrophilic surface with a water contact angle of 54° and the hydrophobic surface with a water contact angle of 133°. Furthermore, the *Staphylococcus aureus* that adhered onto the hydrophobic and superhydrophobic surfaces were more scattered, while the *Staphylococcus aureus* that adhered onto the hydrophilic surfaces tended to gather. After 4 h, similar trends were found, except that the amount of adhered cells on all three surfaces increased. The authors concluded that although the cells were not totally absent on the superhydrophobic surfaces and the amount of adhered cells increased with time, they were much less in quantity and more scattered than those on the hydrophilic and hydrophobic surfaces and could be easily removed.

Privett *et al.*[102] demonstrated that the adhesion of *Staphylococcus aureus* and *Pseudomonas aeruginosa* was reduced significantly on the superhydrophobic coating (water contact angle of 167°) obtained from fluorinated silica colloids. Crick *et al.*[103] reported reduced *Staphylococcus aureus* and *Escherichia coli* adhesion on their AACVD (aerosol assisted chemical vapour deposition) coated superhydrophobic surface (water contact angel of 165°) compared with an uncoated plain glass (water contact angle of 60°) and a dip-coated elastomer glass (water contact angle of 95°). Furthermore, Freschauf *et al.*[104] found a good prevention of *Escherichia coli* growth on their shrink-induced superhydrophobic polystyrene (PS), poly-carbonate (PC) and polyethylene (PE) surfaces and also demonstrated the effectiveness of rinsing on removing bacterial cells. Only 2% of the initial bacterial cells adhered on the superhydrophobic surface. Rinsing removed nearly all the cells with less than 0.1% of the initial bacterial cells remaining on the surface.

On the other hand, Fadeeva *et al.*[105] reported that *Staphylococcus aureus* cells were colonized after 18 h on the

laser ablated superhydrophobic Ti surface though *Pseudomonas aeruginosa* cells did not attach to the surface. The authors suggested that the spherical *Staphylococcus aureus* cells (typically 1 μm in diameter) required a much lower degree of surface contact to adhere compared to the rod-like *Pseudomonas aeruginosa* cells (typically 1–5 μm long and 0.5– 1 μm wide). On the other hand, Sousa *et al.*[106] reported both *Staphylococcus aureus* and *Pseudomonas aeruginosa* colonized on their superhydrophobic poly(L-lactic acid) surface after 24 h and *Pseudomonas aeruginosa* was even able to form a biofilm on the surface. Furthermore, the bacteria were not able to be removed easily by water. However, further discussions on the mechanisms were not given in the paper.

Reducing bacterial adhesion *via* superhydrophobicity is a relatively new topic and has yet to be studied thoroughly and systematically. The majority of the current research is still focusing on investigating the phenomenon and the potential of applying superhydrophobic surfaces to reduce bacterial adhesion. As shown in Table 1, the tested superhydrophobic surfaces are based on different materials processed by different methods. The only parameter that is constant is the contact angle for water, which is over 150° on all the surfaces. The bacterium types tested are limited to *Staphylococcus aureus*, *Escherichia Coli* and *Pseudomonas aeruginosa*. The bacterial adhesion test procedure also differs from study to study. In some studies a bacterial suspension was flown over the samples while in others the samples were immersed in the bacterial suspension, with the incubation time varying between 1 and 24 h. Therefore, it is not surprising that contradictive results could be obtained as the experimental details could significantly affect the results. In order to fully understand the mechanisms of bacterial adhesion on super-hydrophobic surfaces, more bacterium types should be tested and the cell adhesion test procedure should be standardized. On the other hand, more parameters, *i.e.* surface roughness values, morphology, functional group and the free energy from the superhydrophobic surfaces, should also be considered. The interaction between bacterial cells and superhydrophobic surfaces should be systematically studied. The two-stage bacterial adhesion shown in Fig. 8 is not necessarily applicable to superhydrophobic surfaces. However, despite the variations in these experiments, a strong potential for using a super-hydrophobic surface to reduce the initial bacterial adhesion is seen, although further efforts are still required.

4.2 Reducing bacterial adhesion *via* reduced protein adsorption

Despite the variations in the results achieved in the studies on superhydrophobic surfaces, it has been agreed that reduced protein adsorption plays an important role in reducing bacterial adhesion on surfaces. Bacterial adhesion is mediated by different types of interactions which can be nonspecific or specific, for example through an adsorbed protein film.[107] The formation of a protein layer can promote bacterial adhesion and facilitate the formation of a biofilm. It is generally considered that proteins tend to adsorb more favourably onto surfaces with contact angles of 60–90° and on hydrophobic surfaces.[108] However, superhydrophobic surfaces have been found to have low protein adsorption and easy protein
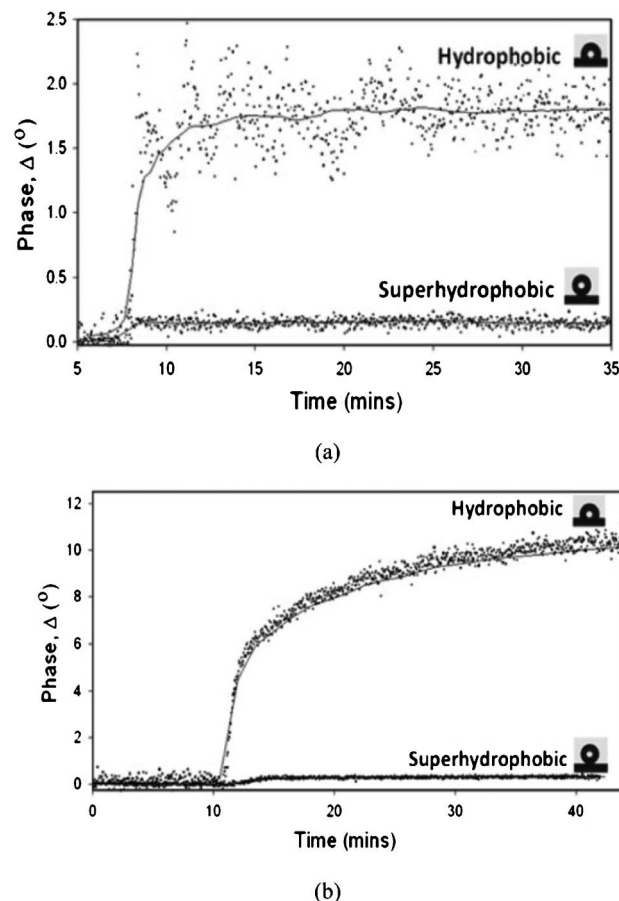

(a)

(b)

Fig. 10 Adsorption profiles of BSA (a) and Fg (b) on hydrophobic and superhydrophobic surfaces. Reprinted with permission from C. P. Stallard, K. A. McDonnell, O. D. Onayemi, J. P. O'Gara and D. P. Dowling, Evaluation of protein adsorption on atmosphere plasma deposited coatings exhibiting superhydro-philic to superhydrophobic properties, *Biointerphases*, 2012, **7**, 31.

detachment,[109,110] thus resulting in a low bacterial adhe-sion.[108,111,112] For example, Stallard *et al.*[108] reported a much lower adhesion of the bovine fibrinogen (Fg) and bovine serum albumin (BSA) proteins on their atmospheric plasma depos-ited superhydrophobic fluorinated siloxane coatings, com-pared with hydrophobic surfaces (see Fig. 10). They also performed bacterial adhesion experiments using *Staphylococcus aureus* to the surfaces before and after a protein adsorption to identify the effect of an adsorbed protein layer on bacterial adhesion. *Staphylococcus aureus* is known to bind specifically to Fg. The results in Fig. 11 revealed that a very low amount of *Staphylococcus aureus* cells attached the super-hydrophobic Ti surface after Fg adsorption compared to the plain Ti surface, as well as to the plain Ti surface after Fg adsorption. It also showed that Fg treatment did not increase the amount of attached *Staphylococcus aureus* cells on the superhydrophobic surface without Fg treatment. This was thought to be due to the lack of an adsorbed Fg protein layer on the superhydrophobic surface even after the Fg treatment. No significant difference in the adhesion between the plain Ti and Fg treated plain Ti surfaces was observed though one

Fig. 11 Attachment of *Staphylococcus aureus* cells to Fg treated and untreated plain Ti and fluorosiloxane coated superhydrophobic (SH) Ti surface. Reprinted with permission from C. P. Stallard, K. A. McDonnell, O. D. Onayemi, J. P. O'Gara and D. P. Dowling, Evaluation of protein adsorption on atmosphere plasma deposited coatings exhibiting superhydrophilic to superhydrophobic properties, *Biointerphases*, 2012, **7**, 31.

could expect the Fg treated plain Ti surface would attract more bacterial cells than the non-treated plain Ti surface. However, the authors did not offer a discussion on this.

4.3 Bacterial adhesion patterns on superhydrophobic surfaces

Although most of the reduced bacterial adhesion on a superhydrophobic surface is shown to be based on a CPU count (bacterial colony producing units) of the adhered cells,

some have studied the bacterial adhesion patterns and its possible mechanism on superhydrophobic surfaces. Truong *et al.*[113] tested the bacterial adhesion on laser ablated superhydrophobic titanium surfaces using strains of *Staphylococcus aureus* CIP 65.8[T], *Staphylococcus aureus* ATCC 25923, *Staphylococcus epidermidis* ATCC 14990[T] and *Planococcus maritimus* KMM 3738. The results showed that each strain preferentially attached to the crevices between the topographical features of the superhydrophobic surface, while the upper regions of the topographical features were cell-free, as shown in Fig. 12.

A mechanism has also been proposed in Fig. 13 where the cells were unable to cross the air–water interface and then began to accumulate in the tri-phase interface that provided the best shelter from water turbulence. Subsequently the bacterial cells slid across the nanoscale bubbles trapped within the nanoscale topographical features. With this mechanism, it can be predicted that the bacterial adhesion would be increased over time due to the replacement of trapped air. It also provides an explanation to the findings reported in reference 101.

4.4 Bacterial adhesion on a wet superhydrophobic surface

Though it is commonly reported that superhydrophobicity and its capability to reduce bacterial adhesion will be lost under submerged conditions over time after the trapped air is completely excluded,[114,115] the naturally superhydrophobic Taro (*Colocasia esculenta*) leaf has been shown to be highly resistant to bacterial adhesion even in completely wet conditions simulated by treating the leaves with 95% ethanol.[116] Fig. 14 shows the *Pseudomonas aeruginosa* adhe-

Fig. 12 SEM images of bacterial adhesion patterns on superhydrophobic Lotus-like Ti surfaces and as-received reference Ti surfaces after incubation for 18 h. Reprinted by kind permission of Taylor & Francis Ltd, from Air-directed attachment of coccoid bacteria to the surface of superhydrophobic lotus-like titanium, V. K. Truong, H. K. Webb, E. Fadeeva, B. N. Chichkov, A. H. F. Wu, R. Lamb, J. Y. Wang, R. J. Crawford and E. P. Ivanova, *Biofouling: the Journal of Bioadhesion and Biofilm Research*, 2012, **28**, 539–550.

Fig. 13 Proposed mechanism by which bacterial cells accumulate at the tri-phase interface on immersed superhydrophobic Ti surfaces. Reprinted by kind permission of Taylor & Francis Ltd, from Air-directed attachment of coccoid bacteria to the surface of superhydrophobic lotus-like titanium, V. K. Truong, H. K. Webb, E. Fadeeva, B. N. Chichkov, A. H. F. Wu, R. Lamb, J. Y. Wang, R. J. Crawford and E. P. Ivanova, *Biofouling*: *the Journal of Bioadhesion and Biofilm Research*, 2012, **28**, 539–550.

sion on a Taro leaf under non-wet and wet conditions after 23 h, together with the morphology of a Taro leaf with the corresponding adhesion force on its nanostructures. Both on the wet and non-wet leaf surface, cells adhered mostly on the boundary between epidermal cell units, displaying circular patterns in Fig. 14a and 14b. The authors suggested that the pattern was attributed to the difference in the surface topographical nanostructures in different densities. The boundary area had a low density of nanostructures with a high adhesion force and thus high cell adhesion, while the edge area of epidermal units had high density of nanostructures with low adhesion force and therefore low cell adhesion (see Fig. 14c). As a conclusion, the authors suggested that properly designed surface nanostructures might be able to reduce bacterial adhesion even in completely wet submerged conditions.

4.5 Other relevant applications

Superhydrophobic surfaces have also been found to have increased resistance to the microbial-induced corrosion (MIC) and fouling in sea water due to its capability to reduce bacterial adhesion.[115,117,118] Zhang *et al.*[115] reported that their superhydrophobic surface had a promising anti-fouling property in the short term. However, after long term exposure to sea water, the superhydrophobic film lost its anti-fouling property. Liu *et al.*[117] found that the marine bacterium *Vibrio natriegens* had only a weak attachment to a superhydrophobic aluminium surface, leading to a significant reduction in the corrosion rate of aluminium due to the lack of *Vibrio natriegens*. Mahalakshmi *et al.*[118] tested their superhydrophobic titanium surface in seawater and found out that microbes did not attach on the surface and the corrosion resistance of titanium in seawater was significantly increased.

4.6 Hybrid solutions in developing antibacterial materials

Although the concept of using superhydrophobicity against bacterial adhesion is green and environmental friendly, the efficiency is rather low, as indicated from the phenomenon that bacteria will adhere to the superhydrophobic surface over

time after the surface become fully wet and the entrapped air is excluded. As aforementioned in the introduction, the use of antibacterial metals and photocatalytic materials form the other parts of the new strategies in developing antibacterial materials besides superhydrophobicity. Attempts at developing hybrid antibacterial materials by combining superhydrophobicity with antibacterial metals or with photocatalysis have been made in order to improve the antibacterial performance while maintaining the green concept of preventing bacterial adhesion in the first place. The efforts of incorporating antibacterial metals such as Ag[119,120] and Cu[17] with superhydrophobicity have been more successful than combining photocatalysis with superhydrophobicity. Tang *et al.*[121] combined superhydrophobicity with photocatalysis by coating a TiO_2 surface with fluorosilane to see the antibacterial effect. Unfortunately the thin surface silane layer would largely stop the photocatalysis. Superhydrophobic ZnO has also been fabricated[122] but antibacterial testing was hardly reported.

5 Concluding remarks

In general, materials properties such as surface energy, wettability (hydrophobicity and hydrophilicity), surface charge, surface chemical composition, surface topography, surface elastic modulus and coating thickness were found to have an influence or a joint influence on the bacterial adhesion on surfaces. Mild hydrophobicity does not always reduce bacterial adhesion.

Different from hydrophobic surfaces, superhydrophobic surfaces have shown a promising capability to reduce bacterial adhesion together with an easy removal of bacteria cells, enabling the superhydrophobic surface to be a new strategy in the antibacterial design. The reduced bacterial adhesion on superhydrophobic surfaces was found to result from the reduced protein adsorption and the entrapped air layer between the bacteria cells and the surface. There are some studies that have investigated the interaction of bacteria cells

Fig. 14 *Pseudomonas aeruginosa* adhesion on a Taro leaf under non-wet conditions in (a) and wet conditions in (b). SEM image of a Taro leaf (left in c) and the corresponding adhesion force map (right in c). Reprinted with kind permission from J. Ma, Y. Sun, K. Gleichauf, J. Lou and Q. Li, Nanostructure on Taro leaves fouling by colloids and bacteria under submerged conditions, *Langmuir*, 2011, **27**, 10035–10040, Copyright (2011) American Chemical Society.

with superhydrophobic surfaces and speculated the possible mechanism. However, the study of bacterial adhesion on superhydrophobic surfaces is not yet sufficiently extensive and systematic. The tested bacteria are rather limited, most commonly with *Staphylococcus aureus*, *Escherichia Coli* and *Pseudomonas aeruginosa*. As bacterial properties play significant roles in the bacteria–material interaction, more bacteria types should be characterized to identify the interaction mechanism on superhydrophobic surfaces. The experimental procedures in the cell adhesion test also differ considerably with many variables (*e.g.* incubation time from 1 h to 24 h) and thus make it very difficult to compare results to draw common

conclusions. In addition to water contact angles, more parameters *e.g.* surface roughness values, morphology, functional group and free energy from the superhydrophobic surfaces should be studied to see their effect on bacterial adhesion. On the other hand, superhydrophobic surfaces are a great concept to change surface properties but unfortunately suffer from a weak durability due to its micro/nano surface structures and fast degradation of surface chemistry. Although initial progress has been reported, more efforts are required to improve the durability of superhydrophobic surfaces.

Certain types of superhydrophobic surfaces have proved to be effective in reducing the bacterial adhesion for up to 24 h.

Over time bacteria cells will colonize on superhydrophobic surfaces after the surfaces have become fully wet and the entrapped air is excluded. However, there is one exciting study existing on the naturally superhydrophobic Taro leaf showing the leaf is still effective against bacteria even under wet conditions. With a further development in the design of the surface structures it may be possible to eliminate the adhesion of bacteria on superhydrophobic surfaces even under wet conditions. Efforts at developing hybrid antibacterial materials by combining superhydrophobicity with antibacterial metals or with photocatalysis have also been attempted. However, the combination of superhydrophobicity, photocatalysis and anti-bacterial metallic materials still require a much longer-term development for success in antibacterial applications.

References

1 J. A. Lichter, K. J. V. Vliet and M. Rubner, Design of antibacterial surfaces and interfaces: polyelectrolyte multilayers as a multifunctional platform, *Macromolecules*, 2009, **42**, 8573–8586.

2 K. Poole, Mechanisms of bacterial biocide and antibiotic resistance, *J. Appl. Microbiol.*, 2002, **92**, 55S–64S.

3 G. McDonnell and A. D. Russell, Antiseptics and disinfectants: activity, action and resistance, *Clin. Microbiol. Rev.*, 1999, **12**, 147–179.

4 A. D. Russell, Bacterial resistance to disinfectants: present knowledge and future problems, *J. Hosp. Infect.*, 1999, **43 (Supp.)**, S453–S464.

5 A. D. Russell, Antibiotic and biocide resistance in bacteria: introduction, *J. Appl. Microbiol.*, 2002, **92**, S1–S3.

6 M. Rai, A. Yadav and A. Gade, Silver nanoparticles as a new generation of antimicrobials, *Biotechnol. Adv.*, 2009, **27**, 76–83.

7 M. T. Hsiao, S. F. Chen, D. B. Shieh and C. S. Yeh, One-pot synthesis of hollow Au_3Cu_1 spherical-like and biomineral botallackite $Cu_2(OH)_3Cl$ flowerlike architectures exhibiting antimicrobial activity, *J. Phys. Chem. B*, 2006, **110**, 205–210.

8 M. Yasuyuki, K. Kunihiro, S. Kurissery, N. Kanavillil, Y. Sato and Y. Kikuchi, Antibacterial properties of nine pure metals: a laboratory study using Staphylococcus aureus and Escherichia coli, *Biofouling*, 2010, **26**, 851–858.

9 C. M. Jones and E. M. V. Hoek, A review of the antibacterial effects of silver nanomaterials and potential implications for human health and the environment, *J. Nanopart. Res.*, 2010, **12**, 1531–1551.

10 A. Gupta and S. Silver, Silver as a biocide: will resistance become a problem, *Nat. Biotechnol.*, 1998, **16**, 888.

11 G. Fu, P. S. Vary and C. T. Lin, Anatase TiO_2 nanocomposites for antimicrobial coatings, *J. Phys. Chem. B*, 2005, **109**, 8889–8898.

12 P. C. Maness, S. Smolinski, D. M. Blake, Z. Huang, E. J. Wolfrum and W. A. Jacoby, Bactericidal activity of photocatalytic TiO_2 reaction: toward an understanding of its killing mechanism, *Appl. Environ. Microbiol.*, 1999, **65**, 4094–4098.

13 J. A. Ibanez, M. I. Litter and R. A. Pizarro, Photocatalytic bactericidal effect of TiO_2 on Enterobacter cloacae: comparative study with other gram (-) bacteria, *J. Photochem. Photobiol., A*, 2003, **157**, 81–85.

14 K. Hashimoto, H. Irie and A. Fujishima, TiO_2 photocatalysis: a historical overview and future prospects, *Jpn. J. Appl. Phys.*, 2005, **44**, 8269–8285.

15 S. In, A. Orlov, R. Berg, F. Garcia, S. Pedrosa-Jimenez, M. S. Tikhov, D. S. Wright and M. Lambert, Effective visible light-activated B-doped and B,N-codoped TiO_2 photocatalysis, *J. Am. Chem. Soc.*, 2007, **129**, 13790–13791.

16 J. Genzer and K. Efimenko, Recent developments in superhydrophobic surfaces and their relevance to marine fouling: a review, *Biofouling*, 2006, **22**, 339–360.

17 A. Berendjchi, R. Khajavi and M. E. Yazdanshenas, Fabrication of superhydrophobic and antibacterial surface on cotton fabric by doped silica-based sols with nanoparticles of copper, *Nanoscale Res. Lett.*, 2011, **6**, 594.

18 B. J. Privett, J. Youn, S. A. Hong, J. Lee, J. Han, J. H. Shin and M. H. Schoenfisch, Antibacterial fluorinated silica colloid superhydrophobic surfaces, *Langmuir*, 2011, **27**, 9597–9601.

19 C. R. Crick, S. Ismail, J. Pratten and I. P. Parkin, An investigation into bacterial attachment to an elastomeric superhydrophobic surface prepared via aerosol assisted deposition, *Thin Solid Films*, 2011, **519**, 3722–3727.

20 Y. Y. Yan, N. Gao and W. Barthlott, Mimicking natural superhydrophobic surfaces and grasping the wetting process: A review on recent progress in preparing superhydrophobic surfaces, *Adv. ColloidInterface Sci.*, 2011, **169**, 80–105.

21 C. Neinhuis and W. Barthlott, Characterization and distribution of water-repellent, self-cleaning plant surfaces, *Ann. Bot.*, 1997, **79**, 667–677.

22 L. Feng, S. Li, Y. Li, H. Li, L. Zhang, J. Zhai, Y. Song, B. Liu, L. Jiang and D. Zhu, Super-hydrophobic surfaces: from natural to artificial, *Adv. Mater.*, 2002, **14**, 1857–1860.

23 T. Young, An essay on the cohesion of fluids, *Philos. Trans. R. Soc. London*, 1805, **95**, 65–87.

24 A. Nakajima, Design of hydrophobic surfaces for liquid droplet control, *NPG Asia Mater.*, 2011, **3**, 49–56.

25 M. Nosonovsky and B. Bhushan, *Multiscale dissipative mechanisms and hierarchical surfaces: friction, superhydrophobicity and biomimetics*, Berlin,Springer, 2008.

26 R. N. Wenzel, Resistance of solid surfaces to wetting by water, *Ind. Eng. Chem.*, 1936, **28**, 988–994.

27 A. Marmur, Super-hydrophobicity fundamentals: implications to biofouling prevention, *Biofouling*, 2006, **22**, 107–115.

28 D. Quere, Rough ideas on wetting, *Phys. A*, 2002, **313**, 32–46.

29 A. B. D. Cassie and S. Baxter, Wettability of porous surfaces, *Trans. Faraday Soc.*, 1944, **40**, 546–550.

30 A. Marmur, The Lotus effect: superhydrophobicity and metastability, *Langmuir*, 2004, **20**, 3517–3519.

31 K. Tadanaga, J. Morinaga, A. Matsuda and T. Minami, Superhydrophobic-superhydrophilic micropatterning on flowerlike alumina coating film by the sol–gel method, *Chem. Mater.*, 1999, **12**, 590–592.

32 B. Bhushan, M. Nosonovsky and Y. C. Jung, Towards optimization of patterned superhydrophobic surfaces, *J. R. Soc. Interface*, 2007, **4**, 643–648.

33 B. Bhushan and Y. C. Jung, Wetting study of patterned surfaces for superhydrophobicity, *Ultramicroscopy*, 2007, **107**, 1033–1041.

34 B. Balu, V. Breedveld and D. Hess, Febrication of "roll-off" and "sticky" superhydrophobic cellulose surfaces via plasma processing, *Langmuir*, 2008, **24**, 4785–4790.

35 M. Miwa, A. Nakajima, A. Fujishima, K. Hashimoto and T. Watanabe, Effects of the surface roughness on sliding angles of water droplets on superhydrophobic surfaces, *Langmuir*, 2000, **16**, 5754–5760.

36 D. K. Owens and R. C. Wendt, Estimation of the surface free energy of polymers, *J. Appl. Polym. Sci.*, 1969, **13**, 1741–1747.

37 Q. Zhao, Y. Liu and E. W. Abel, Effect of temperature on the surface free energy of amorphous carbon films, *J. Colloid Interface Sci.*, 2004, **280**, 174–183.

38 C. J. van Oss, M. K. Chaudhury and R. J. Good, Interfacial Lifshitz-van der Waals and polar interactions in macroscopic systems, *Chem. Rev.*, 1988, **88**, 927–941.

39 T. Nishino, M. Meguro, K. Nakamae, M. Matsushita and Y. Ueda, The lowest surface free energy based on -CF3 alignment, *Langmuir*, 1999, **15**, 4321–4323.

40 E. M. Harnett, J. Alderman and T. Wood, The surface energy of various biomaterials coated with adhesion molecules used in cell culture, *Colloids Surf., B*, 2007, **55**, 90–97.

41 W. Barthlott and C. Neinhuis, Purity of the sacred lotus, or escape from contamination in biological surfaces, *Planta*, 1997, **202**, 1–8.

42 X. Zhang, X. Liu, J. Laakso, E. Levänen and T. Mäntylä, Easy-to-clean property and durability of superhydrophobic flaky γ-alumina coating on stainless steel in field test at a paper machine, *Appl. Surf. Sci.*, 2012, **258**, 3102–3108.

43 X. Zhang, M. Järn, J. Peltonen, V. Pore, T. Vuorinen, E. Levänen and T. Mäntylä, Analysis of roughness parameters to specify superhydrophobic antireflective boehmite films made by the sol–gel process, *J. Eur. Ceram. Soc.*, 2008, **28**, 2177–2181.

44 L. Zhang, Y. Li, J. Sun and J. Shen, Layer-by-layer fabrication of broad-band superhydrophobic antireflection coatings in near-infrared region, *J. Colloid Interface Sci.*, 2008, **319**, 302–308.

45 L. Gao, A. K. Jones, V. K. Sikka, J. Wu and D. Gao, Anti-Icing superhydrophobic coatings, *Langmuir*, 2009, **25**, 12444–12448.

46 L. Mishchenko, B. Hatton, V. Bahadur, J. A. Taylor, T. Krupenki and J. Aizenberg, Design of ice free nanostructured surfaces based on repulsion of impacting water droplets, *ACS Nano*, 2010, **4**, 7699–7707.

47 A. J. Meuler, G. H. McKinley and R. E. Cohen, Exploiting topographical texture to impart icephobicity, *ACS Nano*, 2010, **4**, 7048–7052.

48 R. Truesdell, A. Mammoli, P. Vorobieff, P. van Swol and C. J. Brinker, Drag reduction on a patterned superhydrophobic surface, *Phys. Rev. Lett.*, 2006, **97**, 044504.

49 R. J. Daniello, N. E. Waterhouse and J. P. Rothstein, Drag reduction in turbulent flows over superhydrophobic surfaces, *Phys. Fluids*, 2009, **21**, 085103.

50 M. Nosonovsky and B. Bhushan, Roughness-induced superhydrophobicity: a way to design non-adhesive surfaces, *J. Phys.: Condens. Matter*, 2008, **20**, 225009.

51 Z. Guo, W. Liu and B. Su, Superhydrophobic surfaces: from natural to biomimetic to functional, *J. Colloid Interface Sci.*, 2011, **353**, 335–355.

52 T. Verho, J. T. Korhonen, L. Sainiemi, V. Jokinen, C. Bower, K. Franze, S. Franssila, P. Andrew, O. Ikkala and R. H. A. Ras, Reversible switching between superhydrophobic states on a hierarchically structured surface, *Proc. Natl. Acad. Sci. U. S. A.*, 2012, **109**, 10213.

53 H. M. Shang, Y. Wang, S. J. Limmer, T. P. Chou, K. Takahashi and G. Z. Cao, Optically transparent superhydrophobic silica-based films, *Thin Solid Films*, 2005, **472**, 37–43.

54 A. Tuteja, W. Choi, M. Ma, J. M. Mabry, S. A. Mazzelle, G. C. Rutledge, G. H. McKinley and R. E. Cohen, Designing superoleophobic surfaces, *Science*, 2007, **318**, 1618–1622.

55 A. Tuteja, W. Choi, G. H. McKinley, R. E. Cohen and M. F. Rubner, Design parameters for superhydrophobicity and superoleophobicity, *MRS Bull.*, 2008, **33**, 752–758.

56 L. Feng, Z. Yang, J. Zhai, Y. Song, B. Liu, Y. Ma, Z. Yang, L. Jiang and D. Zhu, Superhydrophobicity of nanostructured carbon films in a wide range of pH values, *Angew. Chem., Int. Ed.*, 2003, **42**, 4217–4220.

57 L. Feng, Y. Song, J. Zhai, B. Liu, J. Xu, L. Jiang and D. Zhu, Creation of a superhydrophobic surface from an amphiphilic polymer, *Angew. Chem., Int. Ed.*, 2003, **42**, 800–802.

58 L. Feng, S. Li, H. Li, J. Zhai, Y. Song, L. Jiang and D. Zhu, Super-hydrophobic surface of aligned polyacrylonitrile nanofibers, *Angew. Chem., Int. Ed.*, 2002, **41**, 1221–1223.

59 L. Jiang, Y. Zhao and J. Zhai, A lotus-leaf-like superhydrophobic surface: a porous microsphere/nanofiber-composite film prepared by electrohydrodynamics, *Angew. Chem., Int. Ed.*, 2004, **43**, 4338–4341.

60 S. Nishimoto and B. Bhushan, Bioinspired self-cleaning surfaces with superhydrophobicity, superoleophobicity, and superhydrophilicity, *RSC Adv.*, 2013, **3**, 671–690.

61 S. S. Latthe, A. B. Gurav, C. S. Maruti and R. S. Vhatkar, Recent progress in preparation of superhydrophobic surfaces: a review, *J. Surf. Eng. Mater. Adv. Technol.*, 2012, **2**, 76–94.

62 Y. K. Lai, Z. Chen and C. J. Lin, Recent progress on the superhydrophobic surfaces with special adhesion: from natural to biomimetic to functional, *J. Nanoeng. Nanomanuf.*, 2011, **1**, 18–34.

63 X. M. Li, D. Reinhoudt and M. Crego-Calama, What do we need for a superhydrophobic surface? A review on the recent progress in the preparation of superhydrophobic surfaces, *Chem. Soc. Rev.*, 2007, **36**, 1350–1368.

64 X. Zhang, M. Honkanen, M. Järn, J. Peltonen, V. Pore, E. Levänen and T. Mäntylä, Thermal stability of the

structural features in the superhydrophobic boehmite films on austenitic stainless steel, *Appl. Surf. Sci.*, 2008, **254**, 5129–5133.

65 X. Zhang, M. Honkanen, V. Pore, E. Levänen and T. Mäntylä, Effect of heat-treating gel films on the formation of superhydrophobic boehmite flaky structures on austenitic stainless steel, *Ceram. Int.*, 2009, **35**, 1559–1564.

66 J. Zimmermann, S. Seeger and F. A. Reifler, Water shedding angle: a new technique to evaluate the water-repellent properties of superhydrophobic surfaces, *Text. Res. J.*, 2009, **79**, 1565–1570.

67 C. R. Crick and I. P. Parkin, Water droplet bouncing – a definition for superhydrophobic surfaces, *Chem. Commun.*, 2011, **47**, 12059–12061.

68 A. Marmur, Underwater superhydrophobicity: theoretical feasibility, *Langmuir*, 2006, **22**, 1400–1402.

69 J. P. Youngblood and N. R. Sottos, Bioinspirited Materials for self-cleaning and self-healing, *MRS Bull.*, 2008, **33**, 732–738.

70 J. Zimmermann, G. R. J. Artus and S. Seeger, Long term studies on the chemical stability of a superhydrophobic silicone nanofilament coating, *Appl. Surf. Sci.*, 2007, **253**, 5972–5979.

71 L. Boinovich, A. M. Emelyanenko and A. S. Pashinin, Analysis of long term durability of superhydrophobic properties under continuous contact with water, *ACS Appl. Mater. Interfaces*, 2010, **2**, 1754–1758.

72 T. Verho, C. Bower, P. Andrew, S. Franssila, O. Ikkala and R. H. A. Ras, Mechanically durable superhydrophobic surfaces, *Adv. Mater.*, 2011, **23**, 673–678.

73 Y. Xiu, Y. Liu, B. Balu, D. W. Hess and C. Wong, Robust superhydrophobic surfaces prepared with epoxy resin and silica nanoparticles, *IEEE Trans. Compon. Packag. Manuf. Technol.*, 2012, **2**, 395–401.

74 Y. Xiu, Y. Liu, D. W. Hess and C. P. Wong, Mechanically robust superhydrophobicity on hierarchically structured Si surfaces, *Nanotechnology*, 2010, **21**, 155705.

75 P. Pareo, G. L. D. Gregorio, M. Manca, M. S. Pianesi, L. D. Marco, F. Cavallaro, M. Mari, S. Pappada, G. Ciccarella and G. Gigli, Ultra lightweight PMMA-based composite plates with robust superhydrophobic surfaces, *J. Colloid Interface Sci.*, 2011, **363**, 668–675.

76 H. Zhou, H. Wang, H. Niu, A. Gestos, X. Wang and T. Lin, Fluoroalkyl silane modified silicone rubber/nanoparticles composite: a superdurable, robust superhydrophobic fabric coating, *Adv. Mater.*, 2012, **24**, 2409–2412.

77 X. Zhu, Z. Zhang, X. Men, J. Yang, K. Wang, X. Xu, X. Zhou and Q. Xue, Robust superhydrophobic surfaces with mechanical durability and easy repairability, *J. Mater. Chem.*, 2011, **21**, 15793–15797.

78 Y. Li, L. Li and J. Sun, Bioinspirated slef-healing super-hydrophobic coatings, *Angew. Chem.*, 2010, **122**, 6265–6269.

79 H. Wang, Y. Xue, J. Ding, L. Feng, X. Wang and T. Lin, Durable, self-healing superhydrophobic and superoleo-phobic surfaces from fluorinated-decyl polyhedral oligo-meric silsesquioxane and hydrolysed fluorinated alkyl silane, *Angew. Chem., Int. Ed.*, 2011, **50**, 11433–11436.

80 A. T. Poortinga, R. Bos, W. Norde and H. J. Busscher, Electric double layer interactions in bacterial adhesion to surfaces, *Surf. Sci. Rep.*, 2002, **47**, 1–32.

81 J. A. Lichter, K. J. V. Vliet and M. F. Rubner, Design of anti-bacterial surfaces and interfaces: polyelectrolyte multi-layers as a multifunctional platform, *Macromolecules*, 2009, **42**, 8573.

82 M. Hermansson, The DLVO theory in microbial adhesion, *Colloids Surf., B*, 1999, **14**, 105–119.

83 Zeta potential an introduction in 30 min, Zetasizer nano series technical note, Malvern Instruments, http://www.malvern.com/.

84 B. A. Jucker, H. Harms and A. J. Zehnder, Adhesion of the positively charged bacterium Stenotrophomonas (Xanthomonas) maltophilia 70401 to galss and Teflon, *J. Bacteriol.*, 1996, **178**, 5472–5479.

85 M. Kiremitci-Gumustederelioglu and A. Pesmen, Microbial adhesion to ionogenic PHEMA, PU abd PP implants, *Biomaterials*, 1996, **17**, 443–449.

86 B. Gottenbos, H. C. Van Der Mei and H. J. Busscher, Initial adhesion and surface growth of Pseudomonas aeruginosa on negatively and positively charged Poly(methacrylates), *J. Mater. Sci.: Mater. Med.*, 1999, **10**, 853–859.

87 Q. Zhao, S. Wang and H. M. Steinhagen, Tailored surface free energy of membrane diffusers to minimize microbial adhesion, *Appl. Surf. Sci.*, 2004, **230**, 371–378.

88 R. E. Baier, Substrata influences on the adhesion of microorganisms and their resultant new surface proper-ties, ed. G. Bitton, K. S. Marshall , in *Adsorption of micro-organisms to surface*, Wiley/Interscience, New York, 1980, pp. 59–104.

89 K. Becker, Detachment studies on microfouling in natural biofilms on substrata with different surface tensions, *Int. Biodeterior. Biodegrad.*, 1998, **41**, 93–100.

90 C. I. Pereni, Q. Zhao, Y. Liu and E. Abel, Surface free energy effect on bacterial retention, *Colloids Surf., B*, 2006, **48**, 143–147.

91 Y. Arima and H. Iwata, Effect of wettability and surface functional groups on protein adsorption and cell adhe-sion using well-defined mixed self-assembled monolayers, *Biomaterials*, 2007, **28**, 3074–3082.

92 J. H. Lee, G. Khang, J. W. Lee and H. B. Lee, Interaction of different types of cells of polymer surfaces with wettability gradient, *J. Colloid Interface Sci.*, 1998, **205**, 323–330.

93 J. Li and W. Zhang, Bacterial behaviours on polymer surfaces with organic and inorganic antimicrobial com-pounds, *J. Biomed. Mater. Res., Part A*, 2008, **88A**, 448–453.

94 M. Raulio, M. Järn, J. Ahola, J. Peltonen, J. B. Rosenholm, S. Tervakangas, J. Kolehmainen, T. Ruokolainen, P. Narko and M. Salkinoja-Salonen, Microbe-repelling coated stain-less steel analysed by field emission scanning electron microscopic and physicochemical methods, *J. Ind. Microbiol. Biotechnol.*, 2008, **35**, 751–760.

95 H. Yang and Y. Deng, Preparation and physical properties of superhydrophobic papers, *J. Colloid Interface Sci.*, 2008, **325**, 588–593.

96 A. Okada, T. Nikaido, M. Ikeda, K. Okada, J. Yamauchi, R. M. Foxton, H. Sawada, J. Tagami and K. Matin, Inhibition of biofilm formation using newly developed coating materials with self-cleaning properties, *Dent. Mater. J.*, 2008, **27**, 565–572.

97 T. R. Scheuerman, A. K. Camper and M. A. Hamilton, Effects of substratum topography on bacterial adhesion, *J. Colloid Interface Sci.*, 1998, **208**, 23–33.

98 A. J. Scardino and R. de NYS, Fouling deterrence on the bivalve shell Mytilus galloprovincialis: a physical phenomenon, *Biofouling*, 2004, **20**, 249–257.

99 A. J. Scardino, E. Harvey and R. de NYS, Testing attachment point theory: diatom attachment on microtextured polyimide biomimics, *Biofouling*, 2006, **22**, 55–60.

100 R. F. Brady and I. L. Singer, Mechanical factors favouring release from fouling release coating, *Biofouling*, 2000, **15**, 73–81.

101 P. Tang, W. Zhang, Y. Wang, B. Zhang, H. Wang, C. Lin and L. Zhang, Effect of superhydrophobic surface of titanium on Staphyococcus aureus adhesion, *J. Nanomater.*, 2011, article ID 178921.

102 B. J. Privett, J. Youn, S. A. Hong, J. Lee, J. Han, J. H. Shin and M. H. Schoenfisch, Antibacterial fluorinated silica colloid superhydrophobic surfaces, *Langmuir*, 2011, **27**, 9597–601.

103 C. R. Crick, S. Ismail, J. Pratten and I. P. Parkin, An investigation into bacterial attachment to an elastomeric superhydrophobic surface prepared via aerosol assisted deposition, *Thin Solid Films*, 2011, **519**, 3722–3727.

104 L. R. Freschauf, J. McLane, H. Sharma and M. Khine, Shrink-induced superhydrophobic and antibacterial surfaces in consumer plastics, *PLoS One*, 2012, **7**, e40987.

105 E. Fadeeva, V. K. Truong, M. Stiesch, B. N. Chichkov, R. J. Crawford, J. Wang and E. P. Ivanova, Bacterial retention on superhydrophobic titanium surfaces fabricated by femtosecond laser ablation, *Langmuir*, 2011, **27**, 3012–3019.

106 C. Sousa, D. Rodrigues, R. Oliveira, W. Song, J. F. Mano and J. Azeredo, Superhydrophobic poly(L-lactic acid) surface as potential bacterial colonization substrate, *AMB Express*, 2011, **1**, 34.

107 I. Banerjee, R. C. Pangule and R. S. Kane, Anti-fouling coatings: recent developments in the design of surfaces that prevent fouling by proteins, bacteria, and marine organisms, *Adv. Mater.*, 2011, **23**, 690–718.

108 C. P. Stallard, K. A. McDonnell, O. D. Onayemi, J. P. O'Gara and D. P. Dowling, Evaluation of protein adsorption on atmosphere plasma deposited coatings exhibiting superhydrophilic to superhydrophobic properties, *Biointerphases*, 2012, **7**, 31.

109 P. Roach, N. J. Shirtcliffe, D. Farrar and C. C. Perry, Quantification of surface bound proteins by fluorometric assay: Comparison with quartz crystal microbalance and amido black assay, *J. Phys. Chem. B*, 2006, **110**, 20572–20579.

110 Y. Koc, A. J. Mello, G. McHale, M. I. Newton, P. Roach and N. J. Shirtcliff, Nano-scale superhydrophobicity: suppres-

sion of protein adsorption and promotion of flow-induced detachmeng, *Lab Chip*, 2008, **8**, 582–586.

111 R. B. Pernites, C. M. Santos, M. Maldonado, R. R. Ponnapati, D. F. Rodrigues and R. C. Advincula, Tunable protein and bacterial cell adsorption on colloidally temperlated superhydrophobic polythiophene films, *Chem. Mater.*, 2012, **24**, 870–880.

112 X. Wang, W. Song, Y. Gan, C. Cheng, C. Xia, P. Jiang, X. Deng, T. Sun and L. Jiang, Superhydrophobic modification of hydroxyapatitie decreased in vitro Streptococcus mutans adhesion and calcium dissolution, *Chin. J. Dent. Res.*, 2009, **12**, 15–20.

113 V. K. Truong, H. K. Webb, E. Fadeeva, B. N. Chichkov, A. H. F. Wu, R. Lamb, J. Y. Wang, R. J. Crawford and E. P. Ivanova, Air-directed attachment of coccoid bacteria to the surface of superhydrophobiclotus-like titanium, *Biofouling*, 2012, **28**, 539–550.

114 J. Zhang, X. Sheng and L. Jiang, The dewetting properties of Lotus leaves, *Langmuir*, 2009, **25**, 1371–1376.

115 H. Zhang, R. Lamb and J. Lewis, Engineering nanoscale roughness on hydrophobic surface – preliminary assessment of fouling behaviour, *Sci. Technol. Adv. Mater.*, 2005, **6**, 236–239.

116 J. Ma, Y. Sun, K. Gleichauf, J. Lou and Q. Li, Nanostructure on Taro leaves fouling by colloids and bacteria under submerged conditions, *Langmuir*, 2011, **27**, 10035–10040.

117 T. Liu, L. Dong, T. Liu and Y. Yin, Investigations on reducing microbiologically-influenced corrosion of aluminium by using superhydrophobic surfaces, *Electrochim. Acta*, 2010, **55**, 5281–5285.

118 P. V. Mahalakshmi, S. C. Vanithakumari, J. Gopal, U. K. Mudali and B. Raj, Enhancing corrosion and biofouling resistance through superhydrophobic surface modification, *Current Science*, 2011, **101**, 1328–1336.

119 M. S. Khalil-Abad and M. E. Yazdanshenas, Superhydrophobic anti-bacterial cotton textiles, *J. Colloid Interface Sci.*, 2010, **351**, 293–298.

120 J. S. Chung, B. G. Kim, S. Shim, S. E. Kim, E. H. Sohn, J. Yoon and J. C. Lee, Silver-perfluorodecanethiolate complexes having superhydrophobic, antifouling, antibacterial properties, *J. Colloid Interface Sci.*, 2012, **366**, 64–69.

121 H. Tang, H. Wang and J. He, Superhydrophobic titania membranes of different adhesive forces fabricated by electrospinning, *J. Phys. Chem. C*, 2009, **113**, 14220–14224.

122 J. Zheng, J. Song, Q. Jiang and J. Lian, Superhydrophobic behaviour and optical properties of ZnO film fabricated by hydrothermal method, *J. Mater. Sci. Technol.*, 2012, **28**, 103–108.