Superhydrophobic and superoleophobic properties in nature

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In this review, we report on superhydrophobic and superoleophobic properties found in nature, which are strongly expected to benefit various potential applications. Mimicry of nature is the easiest way to reproduce such properties because nature has for millennia produced plants, insects and animals able to repel water as well as low surface tension liquids such as oils. The most famous example is the lotus leaf, but we may also consider insects able to walk on vertical surfaces or on the water surface, insects with colored structured wings or insects with antifogging and anti-reflective eyes. Most of the time, nature produces nanostructured waxes to obtain superhydrophobic properties. Very recently, the repellency of oils has been reported in springtails, for example. While several publications have reported the fabrication of superoleophobic surfaces using re-entrant geometry, in all of these publications fluorinated compounds were used because they have high hydrophobic properties but also relatively important oleophobic properties in comparison to hydrocarbon analogs even if they are intrinsically oleophilic. However, nature is not able to synthesize fluorinated compounds. In the case of the springtails, the surface structures consists of regular patterns with negative overhangs. The chemical composition of the cuticles is composed of three different layers: an inner cuticle layer made of a lamellar chitin skeleton with numerous pore channels, an epicuticular structures made of structural proteins such glycine (more than 50%), tyrosine and serine an the topmost envelope composed of lipids such as hydrocarbon acids and esters, steroids and terpenes. This discovery will help the scientific community to create superoleophobic materials without the use of fluorinated compounds.

Introduction

The apparent water contact angle of smooth surfaces (θ_w^Y), described by the Young equation, depends on the solid–vapor, solid–liquid and liquid–vapor surface tensions and does not exceed 125–130°, whatever the surface chemistry [1]. However, many natural surfaces display superhydrophobic properties [2,3]. Such properties are characterized by an apparent water contact angle (θ_w) > 150° and various adhesions of water on the surface determined by dynamic contact angle measurements (hysteresis H and sliding angle α). Intensive surface analyses at a micro and nanoscale have shown the necessity of surface structures. The hydrophobic properties are extremely dependent on the morphology and the topography of surfaces, as described by the Wenzel and Cassie–Baxter equations [4,5]. Indeed, in the Wenzel state ($\cos\theta = r\cos\theta^Y$), the water droplet is in full contact with the surface and θ^Y is amplified by a roughness parameter (r) [4] (Fig. 1a). Superhydrophobic properties can be reached only if $\theta_w^Y > 90°$ (intrinsically hydrophobic materials), but with high H and α due to the increase in the solid–liquid interface. The Cassie–Baxter equation ($\cos\theta = \varphi_s(\cos\theta^Y + 1) - 1$ with φ_s and $(1 - \varphi_s)$ the solid fraction and the air fraction, respectively) can also be used [5] (Fig. 1b). In this last case, the water droplet is suspended on a composite interface made of solid and air trapped between the droplet and the surface. The Cassie–Baxter equation can predict superhydrophobic properties but with low H and α due to the increase in the solid–vapor interface. This equation can also

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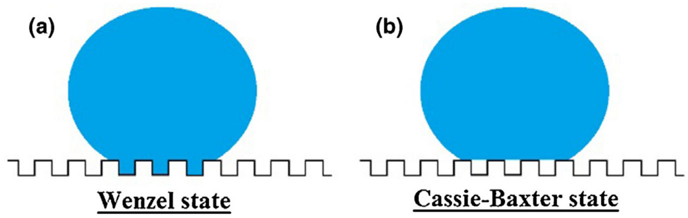

FIGURE 1
Water droplet in (a) the Wenzel state and (b) in the Cassie–Baxter state.

predict the possibility of achieving superhydrophobic properties from intrinsically hydrophilic materials ($\theta_w^Y < 90°$) and even superoleophobic properties from intrinsically oleophilic materials ($\theta_{oils}^Y < 90°$).

Materials with superhydrophobic or superoleophobic properties are in extreme demand due to various potential applications such as in anti-corrosion coatings, anti-icing coatings, liquid-repellent textiles, oil/water separation, nanoparticles assembly, microfluidic devices, printing techniques, optical devices, high-sensitive sensors or batteries [6–14]. In many of these applications, the presence of an air layer trapped inside the surface roughness can reduce the liquid penetration (oil/water separation, anti-fogging), the ion penetration (anti-corrosion, water desalination, batteries), the heat transfer (anti-icing), while the surface roughness can improve the intrinsic properties of the materials (optical, electrical, catalytic properties). It is also extremely important that the superhydrophobic coating is robust, which means the materials keep their properties even after high pressure.

An easier way to fabricate such properties is to mimic nature. Hence, here, we give a brief review of superhydrophobic and superoleophobic properties found in nature.

Superhydrophobic properties in plants

The most famous example of natural superhydrophobic surfaces are lotus leaves (*Nelumbo nucifera*), which are characterized by $\theta_w > 150°$, ultra-low water adhesion (ultra-low H and α) and self-cleaning properties [15] (Fig. 2). The self-cleaning properties (properties to remove dust and particles by the moving of water droplets) are derived from the Cassie–Baxter state (Fig. 2b,c). This property is the consequence of a dual (micro/nano) surface structure (Fig. 2d). The duality is very important to stabilize the Cassie–Baxter state even after pressures corresponding to the impact of rainfall [16]. At the microscale (Fig. 2e) the leaf contains convex cell papilla, while at the nanoscale (Fig. 2f) epicuticular wax (lipid)

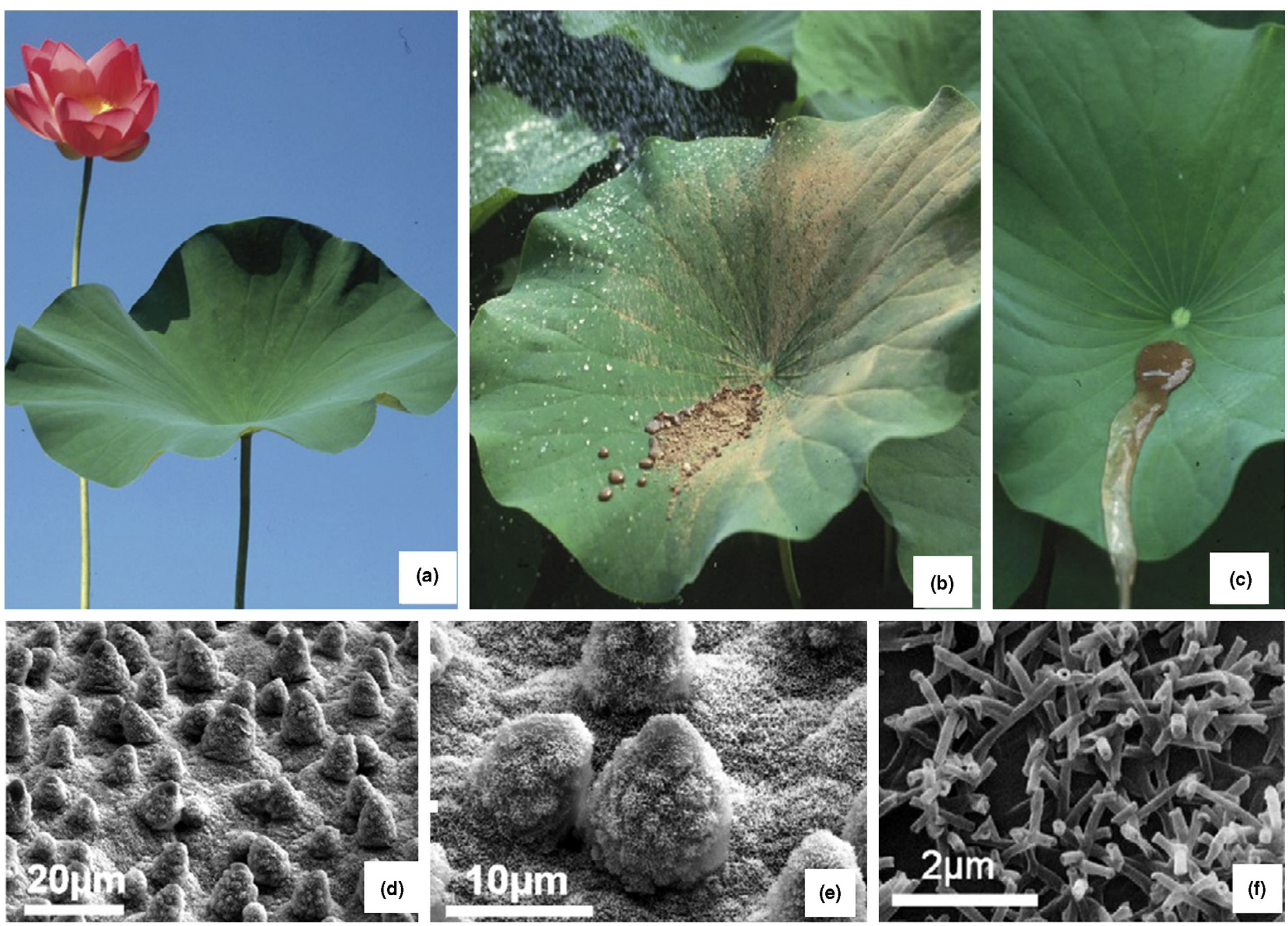

FIGURE 2
Images of a superhydrophobic lotus leaves (*Nelumbo nucifera*) with self-cleaning properties at different magnifications [17].

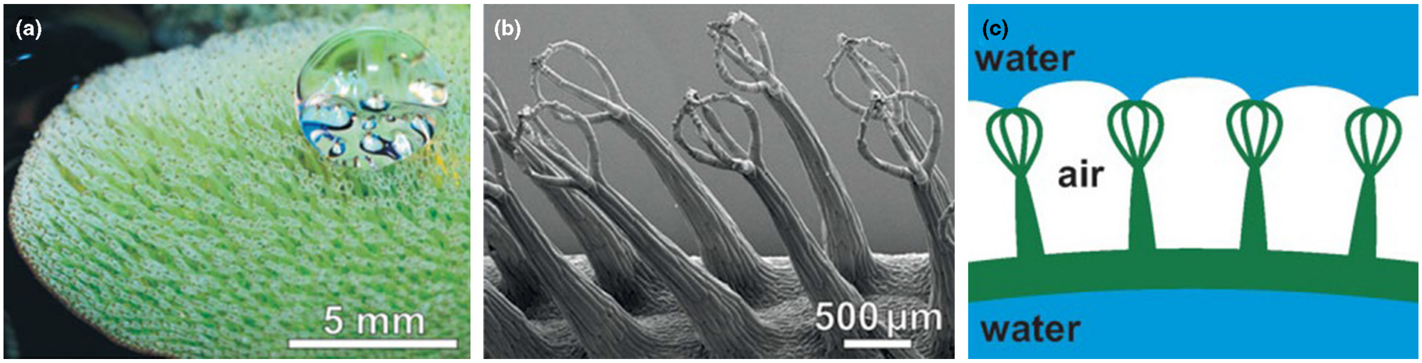

FIGURE 3
Images of a superhydrophobic *Salvinia molesta* at different magnifications. [19], Copyright 2010. Reprinted with permission from Wiley-VCH, Germany.

crystals are observed. Since this discovery, many superhydrophobic plants have been investigated. Barthlott and coworkers studied the surface structures of submersed and floating water plants [17,18]. They found that the plants with submerged leaves are completely wetting with relatively smooth surface cells and no wax crystals. On the other hand, some plants with floating leaves were highly structured. This is the case for plants of the genus *Salvinia*, and in particular *Salvinia molesta*, which present on their surfaces multi-cellular hairs, such as microscopic eggbeater structures with hydrophilic patches [19] (Fig. 3). The hydrophilicity of the patches allows the pinning of the air–water interface (Fig. 3c), which increases the stability of this interface. As a consequence, these structures are able to stabilize the presence of air underwater and be submerged for several weeks. Pedersen *et al.* also reported that *Melilotus siculus*, an annual legume with superhydrophobic leaves, is able to retain gas underwater and achieves photosynthesis even after three days of complete submergence [20,21]. Moreover, this plant is able to survive in saline water because the presence of a gas layer physically separates the seawater from the leaf [22]. This property is extremely interesting for applications in membrane distillation for water desalination. In the case of emergent plants such as lotus leaves, many of the plants were water-repellent with three-dimensional wax crystals. The size of the crystals ranges from 0.5 to 20 μm and the composition is various and includes long chain hydrocarbons and derivatives with carbon chain lengths between 20 and 60 atoms [23–26]. However, Cheng and coworkers also reported that the wax of the lotus leaves is hydrophilic ($\theta_w^Y = 74°$) [27]. Boreyko and Chen also confirmed the hydrophilicity of the lotus leaves by condensation experiments showing that the Wenzel state is the thermodynamically stable state on the lotus leaves and that the Cassie–Baxter state is metastable [28]. Indeed, it is possible to achieve superhydrophobic properties from intrinsically hydrophilic materials as well as superoleophobic properties from intrinsically oleophilic materials [29]. The main requirement was found to be the presence of re-entrant structures, also called multivalued roughness topographies [30], which can strongly pin the liquid–vapor interface [31,32]. The air trapped below re-entrant structures can induce a negative Laplace pressure difference changing the liquid–vapor interface from concave to convex and impede liquid penetration [33].

Land plants also display various surface structures and wettability. For example, the petal of *Rosa montana* consists of convex conical cells with a cuticular nanofolding [17,18]. It was also reported that the petals of red roses possess superhydrophobic properties with high adhesion [34–37] (Fig. 4). The size of the conical cells, also called micropapillae, was 16 μm in diameter and 7 μm in height. It is also interesting to note that the size of both the microstructures and nanostructures of the red petals is larger than that of the lotus leaves ($\varnothing \approx 11$ μm). The authors demonstrated that a water droplet deposited on these surfaces was in the impregnating Cassie–Baxter state (intermediate state between the Wenzel and the Cassie–Baxter states) [38]. Indeed, the water could enter the large spaces between the large micropapillae, but not inside the nanofolds. Similar properties were also reported for peanut leaves [39]. However, the wild pansy (*Viola tricolor*), which possess much closer surface structures than the rose petals, displayed self-cleaning properties [40]. This is probably due to differences in the dimension of the structures ($\varnothing \approx 12.5$ μm and height $h = 40$ μm).

Superhydrophobic leaves containing hairs have also been reported in the literature. While Lady's Mantle was found to have vertical hairs [41], horizontal hairs were observed on ragwort and poplar leaves [42,43]. In the last cases, the white color of the plants leads to high reflectance properties.

To finish with superhydrophobic plants, it is also important to cite the examples of *Strelitzia reginae* and *Oryza sativa* (rice) leaves [44,45]. It was shown that the superhydrophobic properties of

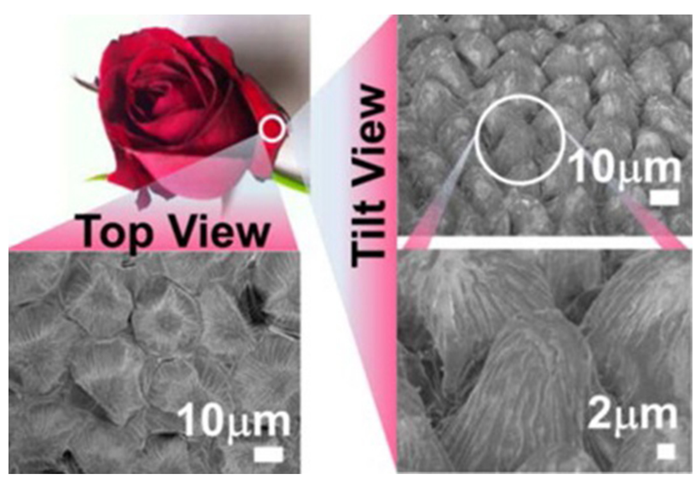

FIGURE 4
Images of a superhydrophobic red rose petal with high adhesion at different magnifications. [36], Copyright 2014. Reprinted with permission from the American Chemical Society, USA.

these leaves are anisotropic. The authors observed the presence of parallel microgrooves on their surface. A water droplet deposited on the leaf remained stuck on it after inclination of the leaf in the direction perpendicular to the microgrooves, but the droplet could be displaced in the direction parallel to the microgrooves.

Moreover, the presence of microgrooves can also reduce the drag of water flux, if in the same direction [46–48], as observed in superhydrophobic microfluidic channels [49].

Superhydrophobic properties in animals

The superhydrophobicity of insect wings is an advantage to reduce the dust/particle contamination and to enhance their flight capability. The group of Barthlott studied the surface structures and wettability of 97 insect wings [50]. They found different families with highly hydrophobic wings including mayflies, dragonflies, stoneflies, lacewings, scorpionflies, alderflies, caddisflies, butterflies, moths and flies [50], as reported by Watson and coworkers for termite wings [51]. Various morphologies were reported, such as cloth-like microstructures, hairs or scales. They also found that the transparent wings of cicada are due to a single level of roughness consisting of regular patterns of nanopillars [50], confirming works reported by Yoshida *et al.* on the transparency of hawkmoth wings (*Cephonodes hylas*) [52]. Indeed, it is possible to have both superhydrophobic and transparent properties by playing on the size of the nanostructures, as the decrease in the transparency is due to the light scattering inside the surface roughness. Sun *et al.* also analyzed the wings of 15 species of cicada [53,54] (Fig. 5). They observed differences in the homogeneity of the nanodomes as well as differences in their diameter ($\varnothing$), height (h) and spacing (s). The highest water-repellent properties were obtained for *Terpnosia jinpingensis* for which $\varnothing = 141$ nm, $h = 391$ nm and $s = 46$ nm. However, a water droplet deposited on these surfaces remained pinned on it, indicating high adhesion (impregnating Cassie–Baxter state). By contrast, Watson *et al.* also reported that the wings of another species of cicada (*Psaltoda claripennis*) with $h \approx 200$ nm and $s \approx 200$ nm were superhydrophobic but with ultra-low adhesion for particles [55]. A natural extension of investigations of air-borne particle adhesion with insect wings as suggested by the studies of Watson *et al.* was the examination of solid contacts of insect cuticle under aqueous conditions. Such studies include those by Ivanova *et al.* demonstrating that cicada wings possess the ability to selectively kill Gram-negative bacteria, while Gram-positive bacteria were not killed [56]. Hence, nanostructured surfaces can open new strategies to develop bactericidal surfaces without biocides.

The chemistry of superhydrophobic insect wings has also been investigated by several research groups. For example, Ivanova *et al.* showed that dragon fly wings are coated by waxes, as observed in superhydrophobic leaves [57,58].

As observed in cicada wings, the presence of highly ordered nanostructures can also lead, in certain cases, to colored as well as iridized materials, without the presence of dyes, if the nanostructures can diffract the light and induce interference effects [59]. The color of the material is directly dependent on the size of the structures [60–62]. The group of Goodwyn studied the structures of different butterflies having hydrophobic or superhydrophobic properties and different colors [61]. While the scales of the transparent butterfly wings of the genus *Parnassius glacialis* (Papilionidae) displayed no clear pattern (Fig. 6a–c), the white translucent regions of *Parantica sita* (Nymphalidae) (Fig. 6d–f) were highly ordered and organized in lines forming periodic and parallel porous microstructures. Prum *et al.* also demonstrated that the color of twelve butterflies (lepidopteran species) is due to

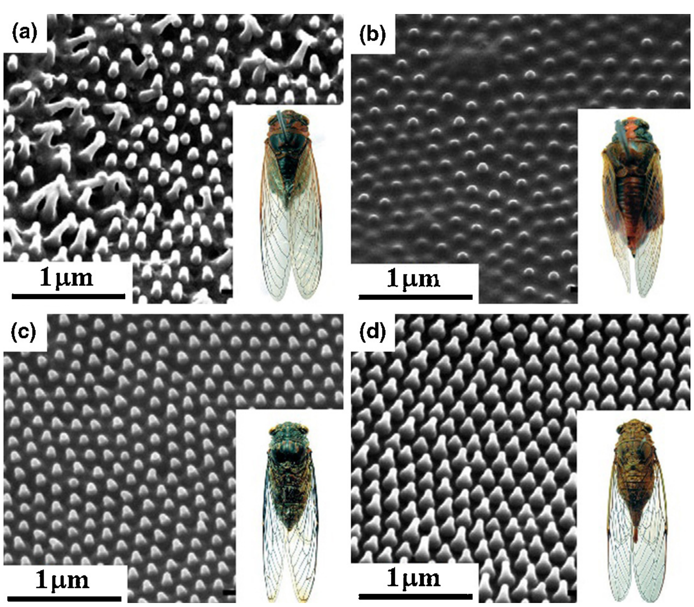

FIGURE 5

Images of the nanostructures present of different species of cicada [53].

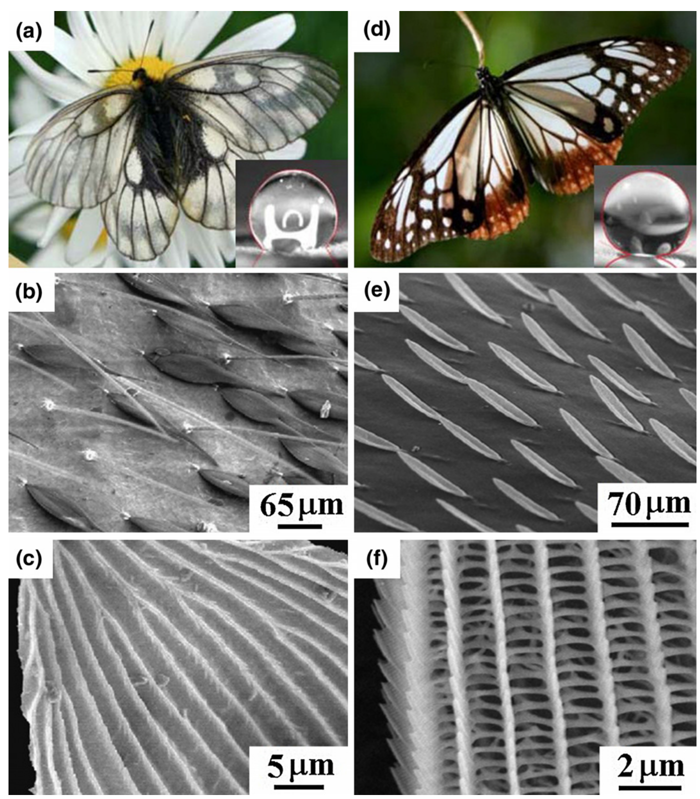

FIGURE 6

Images at different magnification of a transparent butterfly wings of *Parnassius glacialis* and a white translucent of *Parantica sita*. [61], Copyright 2009. Reprinted with permission from Springer, Germany.

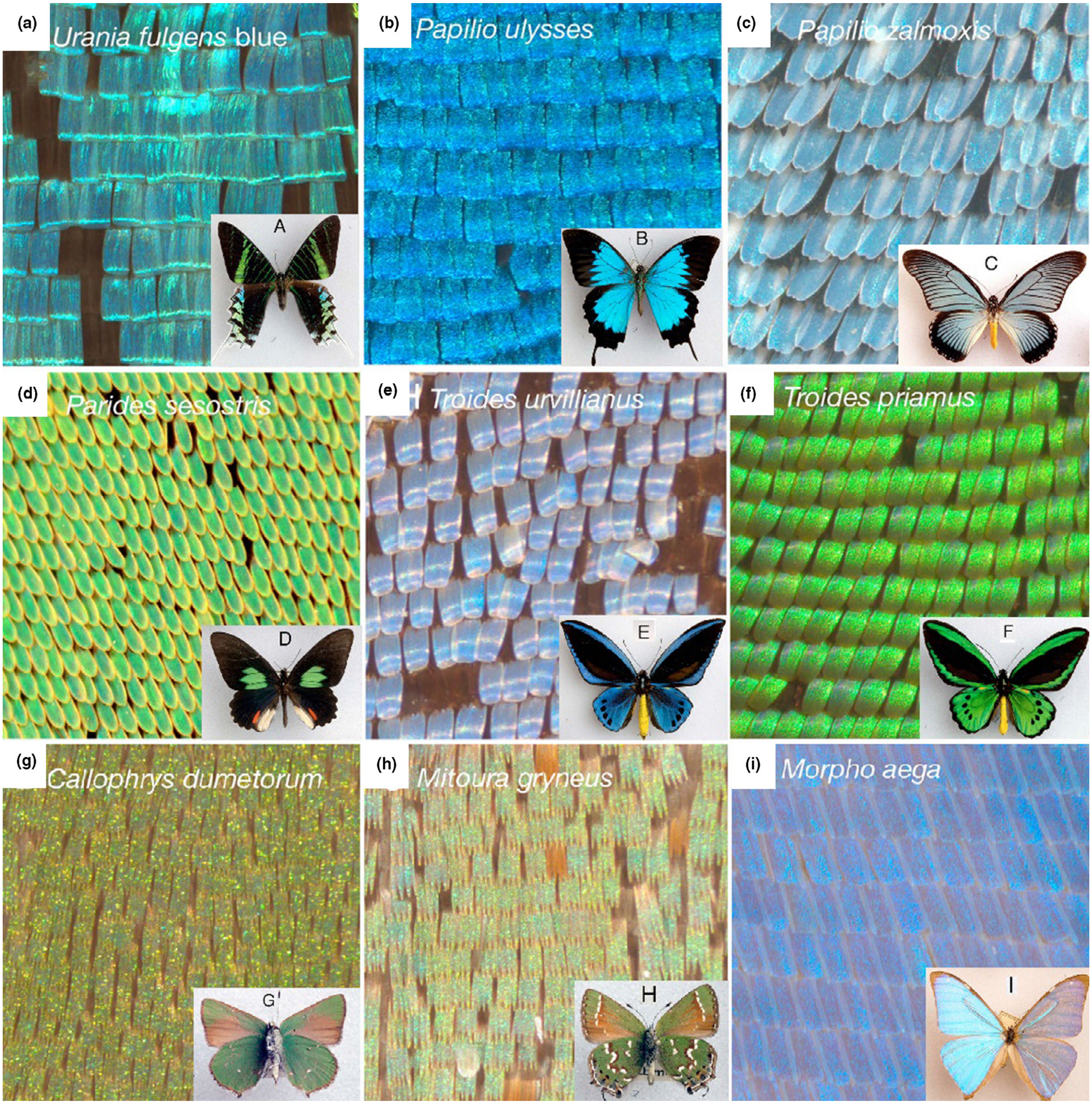

FIGURE 7

Images of the different scales and colors observed in different species of butterflies [63].

appropriate nanostructures in their scales producing visible colors, such as blue, green, or violet [63] (Fig. 7). Moreover, at the microscale, the scales of butterflies, such as *Morpho aega*, overlap in only one direction. As a consequence, the wings of these species are superhydrophobic but with directional adhesion, also called anisotropicity [64]. When a water droplet is deposited on the wing, it can roll off the surface only if the wing is inclined in one direction [46–48].

Moreover, it is possible to combine other properties such as anti-reflective properties and anti-fogging properties. In nature, highly ordered structures at both the micro and the nanoscale were reported for anti-reflective and anti-fogging properties. Anti-reflective properties were observed in fly and moth eyes such as *Cameraria ohridella* [65–67] (Fig. 8a–d). These eyes consist of hexagonal facets (ommatidia). At the nanoscale, the facets contain periodic arrays of protuberances, also called nano-nipples,

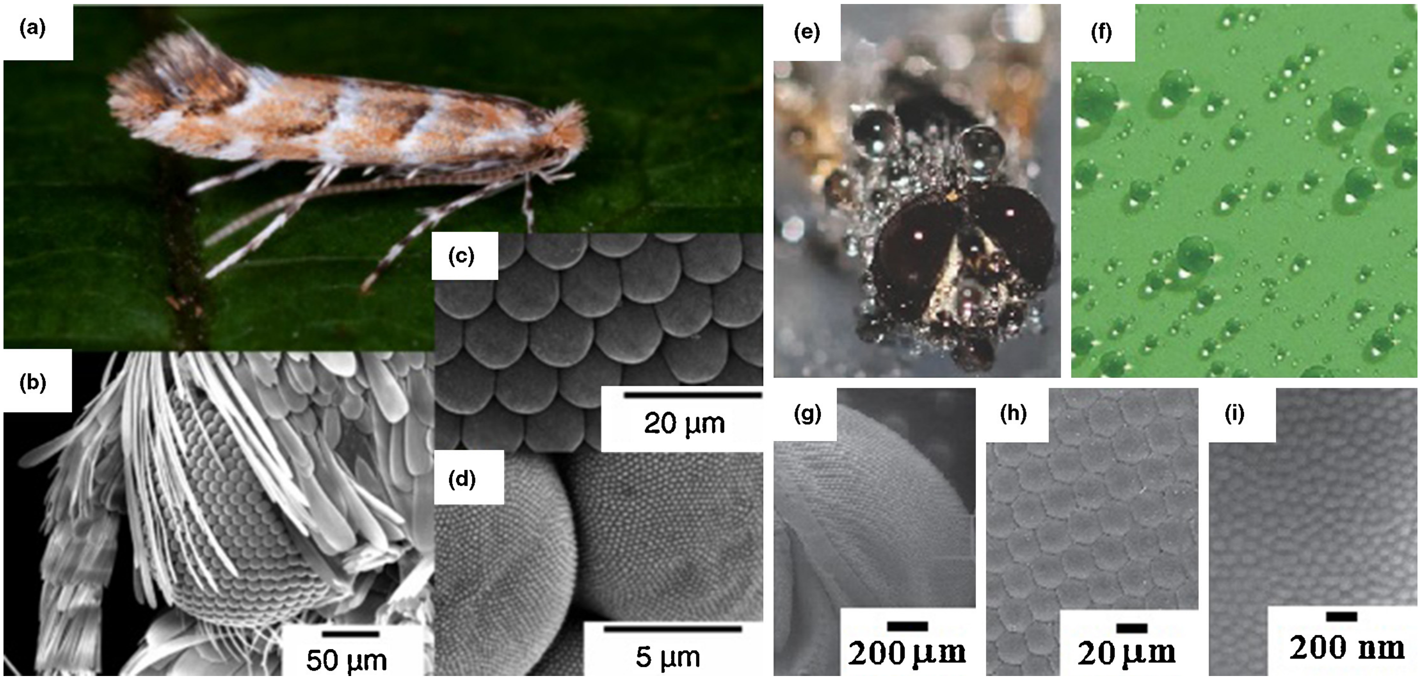

FIGURE 8
Images at different magnifications of (a–d) anti-reflective moth eyes and (e–i) anti-fogging fly eyes. [65], Copyright 2012. Panels (a–d) reprinted with permission from Institute Of Physics, United Kingdom. [70], Copyright 2014. Panels (e–i) reprinted with permission from Wiley-VCH, Germany.

with a diameter of 200 nm and a height of 70–80 nm. Such properties are extremely important for applications in solar cells, for example [68]. Relatively close nanostructures were found to be responsible for the anti-fogging properties of mosquito and fly eyes [69,70] (Fig. 8e–i). Indeed, the formation of fog appears by condensation of vapor (nuclei > 190 nm) into water droplets and can reduce the visibility of the eye. Hence, to induce the repellency of the condensation nuclei, it is important to have surface structures of lower size (<190 nm), as observed in mosquito and fly eyes.

The feet of many insects are also superhydrophobic. Geckos are able to climb on vertical surfaces due to their feet having high solid–solid adhesion [71–73]. This behavior is explained by the presence of well-aligned microscopic hairs, called setae, on their feet (Fig. 9). Their length was 20–70 μm and their diameter 3–7 μm. Moreover, each setae is also split into hundreds of nanometric spatula (100–200 nm in diameter). These setae are composed of α- and β-keratins, which could also affect the adhesion. Hence, the high adhesion is due to van der Waals interactions and capillary forces, which are amplified by the surface area of the rough foot. When a water droplet was deposited on a gecko foot, superhydrophobic properties were reported with $\theta_w \approx 160^\circ$ [74–76]. However, the water droplet remained stuck on the foot even if turned upside down. As a consequence, gecko feet are superhydrophobic but with extremely high water adhesion (sticky behavior). The group of Jiang found that the adhesive forces of the gecko foot are in the range 10–60 μN [74].

Many insects, such as water striders, are able to slide on the surface of water [77,78] (Fig. 10). Indeed, while the world of humans is governed by gravity, that of water-walking arthropods is dominated by surface tension. The surface tension of water (72 mN/m) is responsible for the buoyancy of the insect, which depends on its weight and the presence of air trapped by the roughness [79–81]. Indeed, these insects sink if they are put on the surface of low surface tension liquids such as oils or surfactant solutions.

The property to walk on water is in part due to the presence of hairs of 30 μm in length and about 1 μm in base diameter on theirs legs (Fig. 10g–i). The hairs are composed of waxes with $\theta_w^Y > 100^\circ$. These conditions are important to maintain superhydrophobic properties with low adhesion (Cassie–Baxter state) and to trap a high volume of air between the hairs, also allowing resistance to the impact of raindrops. Their hairs are tilted relative to the body surface, which increases the resistance to fluid impregnation and maximizes the propulsive thrust.

Moreover, the thorax has a relatively fine inner hair layer (microtrichia) allowing the formation of a plastron (air trapped by their hairs) against hydrostatic pressures [82]. This property allows these insects to resist submersion underwater and also to breathe underwater [83–85]. Usually the collapse of the plastron arises at pressures in the range 1–5 atms, corresponding to a depth of 10–50 m.

Superhydrophobic properties with gradient wettability in nature

In nature, water harvesting is often necessary to survive, especially in a hot environment. Many strategies have been found in nature for the collection of water, such as the use of both superhydrophobic and superhydrophilic areas to collect and guide water. Shirtcliffe *et al.* reported that plants such as *Alchemilla mollis*, *Echeveria*, *Lupin regalis* and *Euphorbia* have superhydrophobic leaves but with highly hydrophilic central zones, which is due to different surface structures and chemistry [86]. Here, the

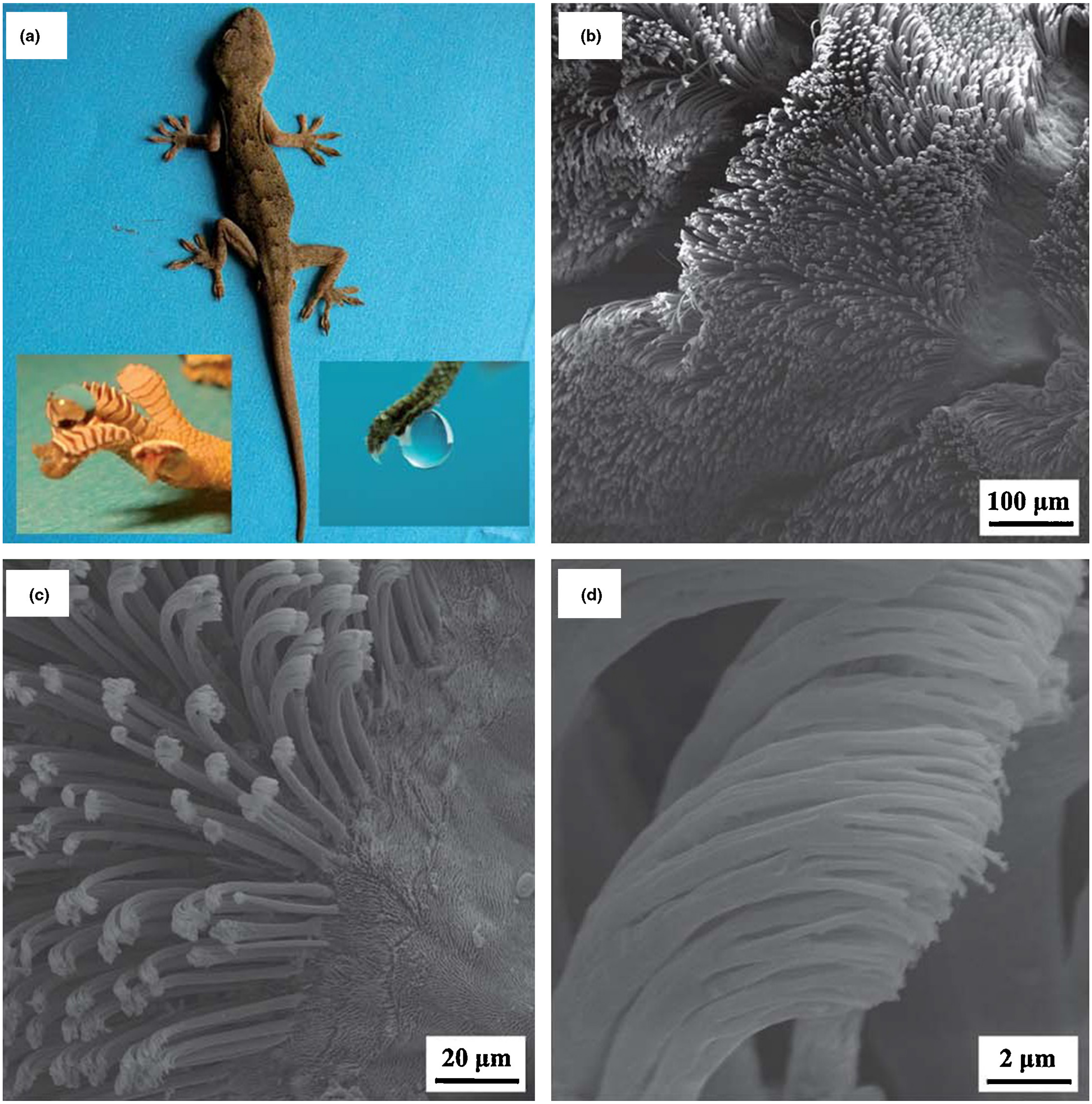

FIGURE 9
Images of superhydrophobic gecko foot with high adhesion at different magnifications, able to walk on vertical surfaces. [74], Copyright 2012. Reprinted with permission from Royal Society of Chemistry, United Kingdom.

possibility to collect water is due the presence of superhydrophobic zones but with a 'sticky' state, as observed on the surface of red roses. Then, when the size of the droplets becomes critical, they roll off the leaf until they reach the stem. The authors also reported the possibility of guiding water by creating superhydrophilic grooves surrounded by superhydrophobic walls to channel the water. In a similar manner, Namib Desert beetles *Stenocara* sp. were found to be able to collect water from early-morning fogs allowing them to survive in an extremely hot environment [87,88]. The authors showed that this ability is due to the presence of superhydrophobic waxy elytra covered by hydrophilic separated bumps. When the droplets become sufficiently big, they roll down into the beetle's mouth.

The group of Jiang also reported than the cactus *Opuntia microdasys*, which originates from the Chihuahua Desert, can also collect water from fog thanks to their spines [89–92]

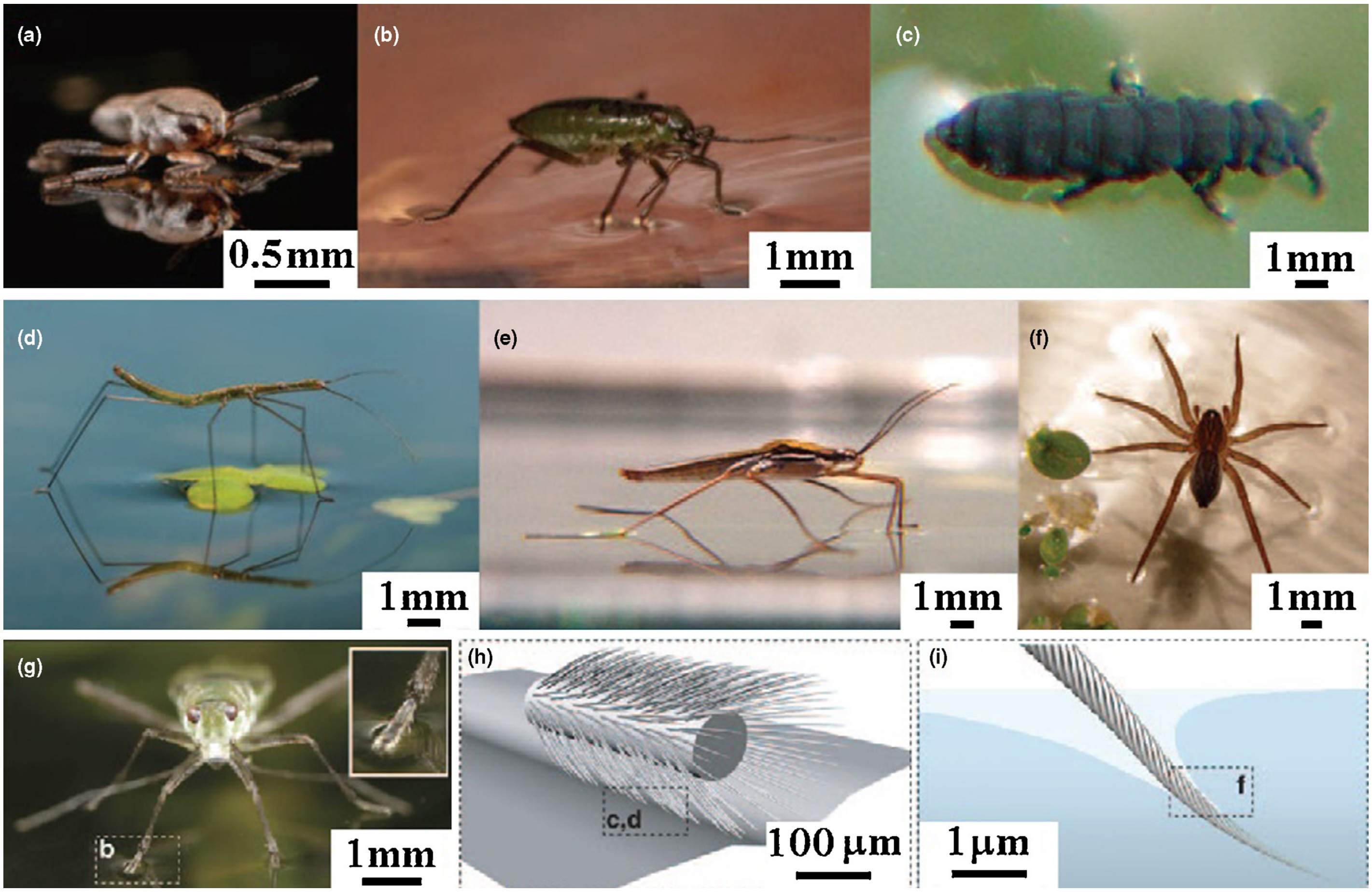

FIGURE 10

(a–f) Images of different water-walking arthropods; (g–i) images of a leg at different magnifications [77].

(Fig. 11). The authors demonstrated that these spines contain microgrooves with a higher roughness near the tip than near the base, leading to a wettability gradient. Similar observations were reported for the endemic Namib Desert grass *Stipagrostis sabulicola*, which consists of stiff culms with heights of up to 2 m [93]. The plants are able to guide water thanks to grooves parallel to the axis of the plant. *Cotula fallax* was also reported to be able to extract water from fog due to a 3D arrangement formed by its leaves and fine hairs covering them [94]. We can also cite the water-collecting ability of the cribellate spider *Uloborus walckenaerius* using silk constituted of periodic spindle-knots made of nanofibrils [95,96].

Underwater superoleophobic properties in nature

The group of Jiang observed that the structure of the lotus leaf in contact with water is different to that in contact with air. They showed that the surface in contact to water is composed of large micropapillae covered with nanogrooves, similar to the structures observed on the surface of red rose [97]. Moreover, these surfaces in contact to water were found to be superoleophobic underwater. Indeed, it is known that fishes and sharks are protected from the pollution induced during oil spills even if they are immerged in water. This property is called underwater superoleophobicity and corresponds to a solid–liquid (water)–liquid (oil) interface. For example, the group of Jiang reported the unique behavior of *Navodon septentrionalis* filefish skin, which displayed anisotropic underwater oleophobicity [98] (Fig. 12a–c). An oil droplet deposited underwater on the surface could roll in the head-to-tail direction but was pinned in the opposite direction. This behavior is due to the presence on the skin of hook-like spines oriented in one direction. The anisotropic underwater oleophobicity is an advantage to survive in oil spilled seawater by avoiding the accumulation of oil on the head.

Bhushan *et al.* also reported on the unique behavior of the shark skin [47,99]. The shark skin is covered by non-packed tooth-like scales also called dermical denticles (Fig. 12d,e). The particular nature of these scales is that they are ribbed with longitudinal grooves. Because the grooves are aligned parallel to the water flow, the speed of the shark is enhanced by the reduction of vortex formation. Hence, the presence of these structured scales allows a reduction in drag when the shark moves [100].

However, if these surfaces are superoleophobic underwater, they are oleophilic when the media is air.

Superoleophobic properties in nature

Following the Young equation [1] and as a consequence the Wenzel and Cassie–Baxter equations, it is much more difficult to impede the wetting of low surface tension liquids such as

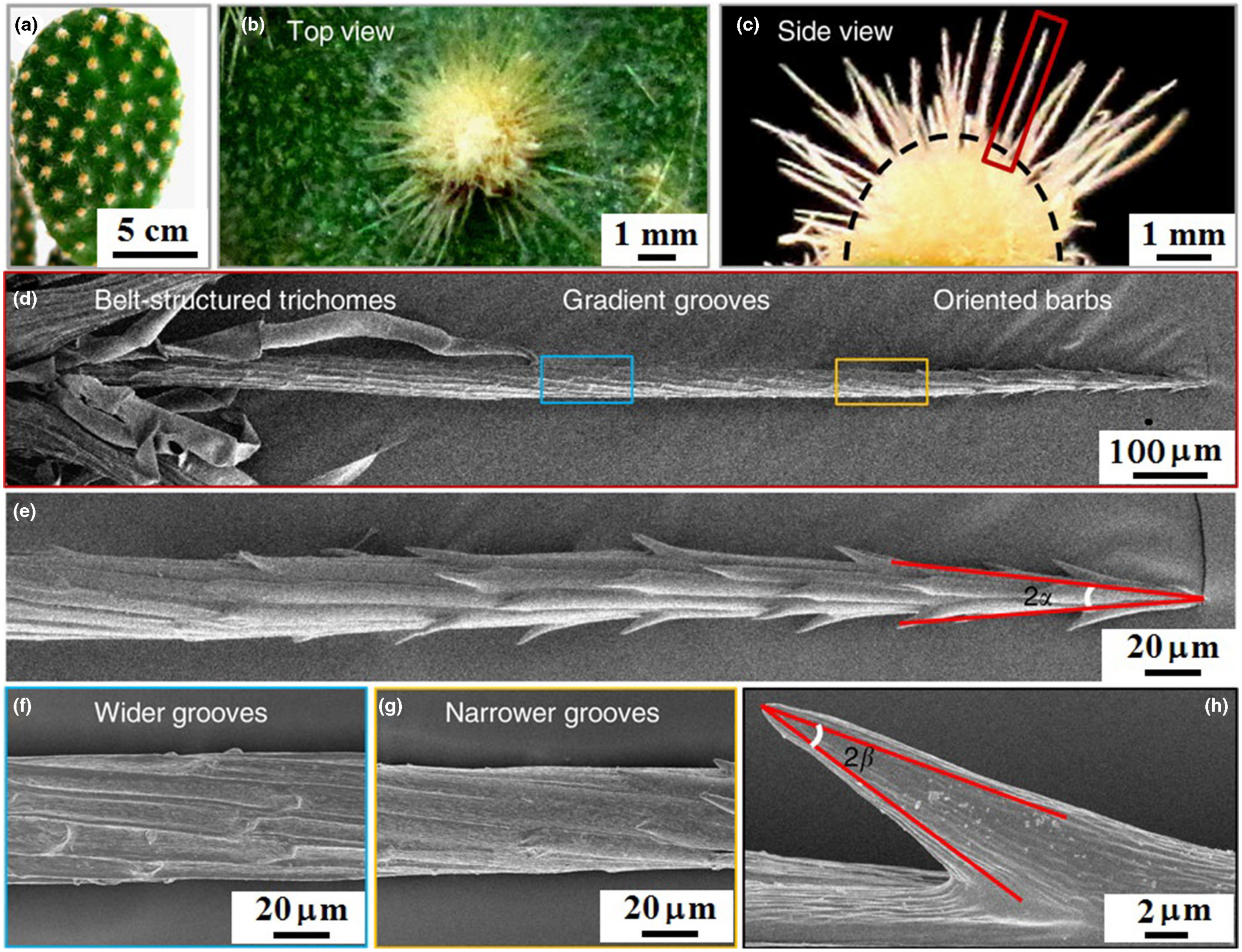

FIGURE 11

(a–f) Images at different magnifications of cactus spines with gradient wettability to collect water. [89], Copyright 2012. Reprinted with permission from Nature Publishing Group, United Kingdom.

oils than water [4,5]. Previous studies have shown that it is possible to form superhydrophobic surfaces from hydrophilic materials as well as superoleophobic surfaces from oleophilic materials combining surface structures with re-entrant curvatures, also called multivalued roughness topographies, such as overhangs, T-like structures or mushroom-like structures [29]. These possibilities can be predicted with the Cassie–Baxter equation as described by Marmur: $\cos\theta = r_f f \cos\theta^Y + f - 1$ where r_f is roughness ratio of the wet surface, f is the solid fraction and $(1 - f)$ is the air fraction [30]. With re-entrant structures, the liquid wets the top of the structures but is highly pinned underneath the re-entrant structures as reported by Law and co-workers [31,32]. The air trapped below re-entrant structures can induce a negative Laplace pressure difference changing the liquid–vapor interface from concave to convex, which is a key parameter to impede liquid penetration [33]. Depending on the geometrical parameters of structures, it is possible to control liquid penetration and as a consequence their adhesion forces.

In the literature, perfluorinated compounds are always used to fabricate superoleophobic materials because they have high hydrophobic properties while the oleophobic properties are relatively important, in comparison to hydrocarbon analogs, even if they are intrinsically oleophilic ($\theta^Y_{oils} < 90°$) [32,101–103]. However, nature is not able to synthesize perfluorinated materials. Hence, the discovery of superoleophobic properties in nature is extremely interesting in respect to finding other alternatives to perfluorinated compounds for the synthesis of superoleophobic properties.

Gorb and Rokitov reported the superoleophobic properties of leafhoppers (Insecta, Hemiptera, Cicadellidae) [104]. These insects produce highly structured particles, called bronchosomes, to uniformly and densely coat their integuments (Fig. 13). These structures protect them from contamination, as well as from getting trapped by their liquid exudates used to feed from plant sap. They are loosely attached to their structures and are erodible, which can reduce the risk of being captured by predators using adhesive substances. These spherical particles have a

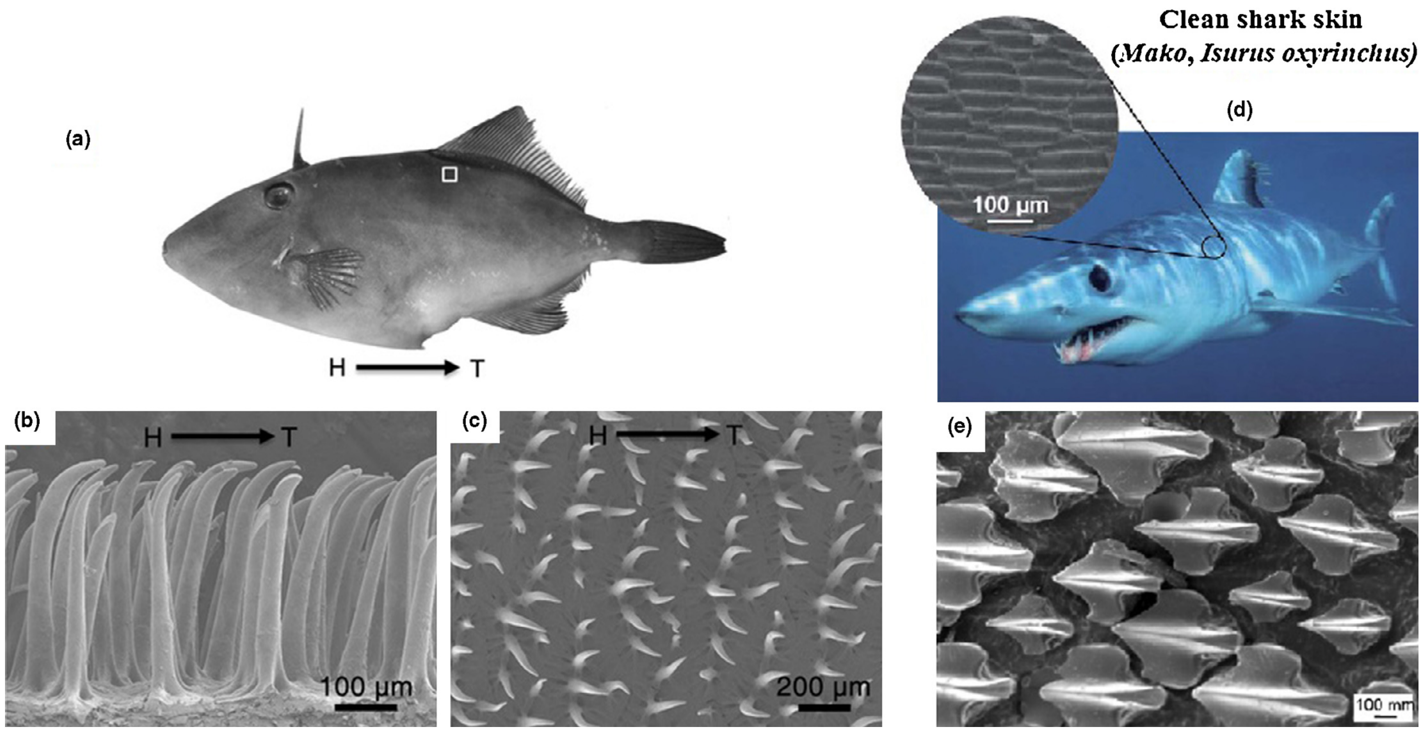

FIGURE 12

(a–f) Images at different magnifications of underwater superoleophobic (a–c) *Navodon septentrionalis* filefish and (d,e) shark skin. [98], Copyright 2014. Panels (a–c) reprinted with permission from Wiley-VCH, Germany. [47], Copyright 2013. Panels (d,e) reprinted with permission from Royal Society of Chemistry, United Kingdom.

hollow core (200–700 nm in diameter) and a honeycomb shape (pentagonal or hexagonal structure). These structures contain re-entrant curvatures responsible for the superoleophobic properties, as reported in the literature [29–33]. It is extremely interesting to notice that these structures are composed of proteins. Hence, it is extremely interesting to find protein structures, which are quite polar molecules, which can be used to reach superoleophobic properties. Here, the bronchosomes were able to repel water with $\theta = 164.9–172.3^{\circ}$, ethylene glycol with $\theta = 152.7–164.1^{\circ}$, diiodomethane with $\theta = 148.2–156.0^{\circ}$, but not able to repel ethanol.

One of the most important examples of natural species with superoleophobic properties was reported by the group of Werner [105–109]. They studied the cuticle micro/nano structures of 40 different species of collembola, also called springtails (Fig. 14). These insects are skin-breathing arthropods and live in a soil environment. The authors showed that to survive in their environment they have developed robust superoleophobic properties on their cuticles due to highly ordered structures and, more precisely, hexagonal or rhombic comb-like patterns. The superoleophobic properties are due to the negative overhang in the profile of the ridges and granules, which induces a strong pinning of the three-phase contact line of a liquid deposited on the surface (even low surface tension liquids). As a consequence, an extremely high energy barrier (dependent on the liquid surface tension) is formed to stabilize the Cassie–Baxter state. This energy also highly depends on the shape of the cavities. Here, the surfaces could resist the wetting of polar and non-polar liquids such as water, methanol, ethanol, hexadecane and tridecane but could not resist dodecane or hexane. They could resist the immersion in these polar and non-polar liquids by forming a very stable plastron, even at elevated pressures (>3.5 atm) and also resist to bacterial adhesion. Very recently, the authors the chemical composition of nanostructured cuticle surface of the collembola *Tetrodontophora bielanensis* [109]. They observed that the cuticle is composed of three different layers. The inner cuticle layer is made of a lamellar chitin skeleton with numerous pore channels. The epicuticular structures of the cuticle are made of structural proteins such glycine (more than 50%), tyrosine and serine. The topmost envelope is composed of lipids such as hydrocarbon acids and esters, steroids and terpenes.

These discoveries open new strategies to develop superoleophobic surfaces without fluorinated materials.

Conclusion

Here, we have reviewed superhydrophobic and superoleophobic properties found in nature. Such properties are in extremely high demand for their various potential applications. The easiest way to fabricate such materials is to mimic nature. Indeed, nature has produced many plants, insects and animals able to repel water, as well as low surface tension liquids such as oils. We show that many species are able to repel water; the repellency of oils has very recently been reported in springtails, for example. Several publications have already reported on the creation of super repelling surfaces using re-entrant geometry, but in all these publications fluorinated compounds were used because they have high hydrophobic properties while having relatively important oleophobic properties in comparison to hydrocarbon

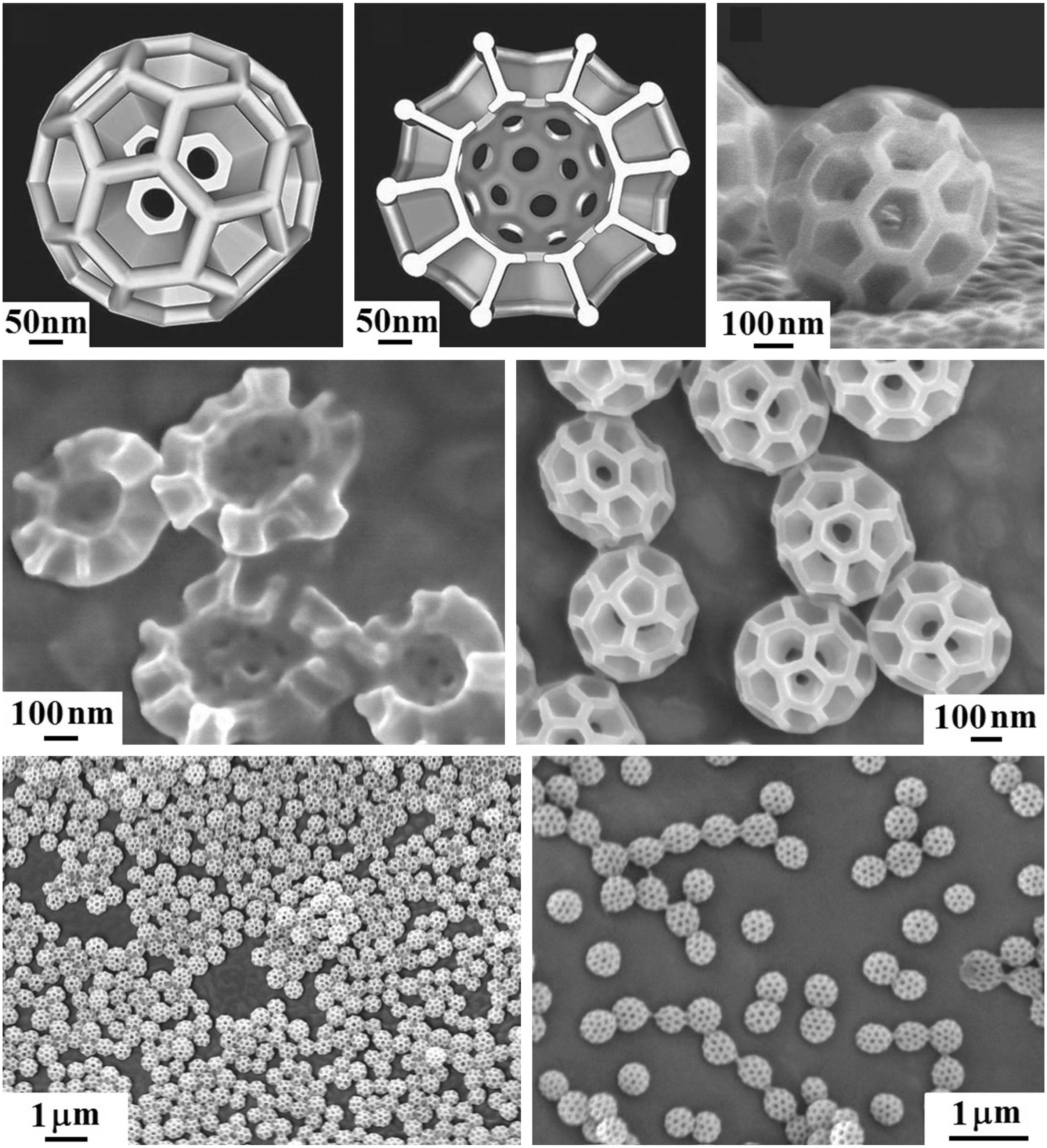

FIGURE 13

Images at different magnifications of superoleophobic bronchosomes present at the surface of leafhoppers. [104], Copyright 2013. Reprinted with permission from The Royal Society, United Kingdom.

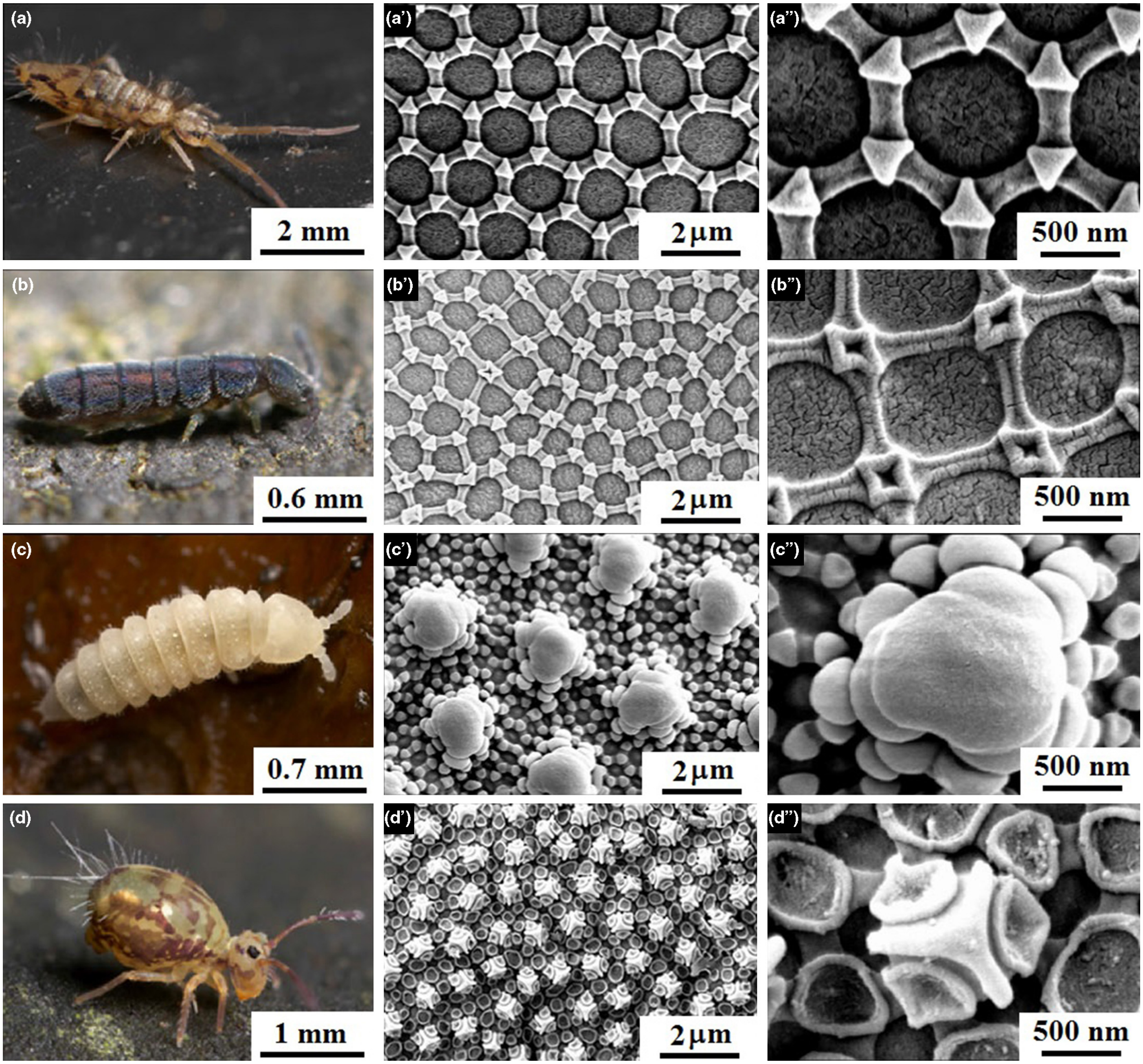

FIGURE 14

Images at different magnifications of different species of superoleophobic springtails. [106], Copyright 2013. Reprinted with permission from Springer, Germany.

analogs, even if they are intrinsically oleophilic ($\theta^{Y}_{oils} < 90°$). However, nature is not able to synthesize perfluorinated chains. This is why it is extremely surprising to find insects with these properties. In the case of the springtails, the surface structures consists of regular patterns with negative overhangs. The authors reported a chemical composition of the cuticles composed of three different layers: an inner cuticle layer made of a lamellar chitin skeleton with numerous pore channels, an epicuticular structures made of structural proteins such glycine (more than 50%), tyrosine and serine an the topmost envelope composed of lipids such as hydrocarbon acids and esters, steroids and terpenes. Hence, the determination of their surface chemistry opens new strategies to develop superoleophobic materials without the use of fluorinated compounds.

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