REVIEW

ADVANCED MATERIALS

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Bio-Inspired, Smart, Multiscale Interfacial Materials**

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In this review a strategy for the design of bioinspired, smart, multiscale interfacial (BSMI) materials is presented and put into context with recent progress in the field of BSMI materials spanning natural to artificial to reversibly stimuli-sensitive interfaces. BSMI materials that respond to single/dual/multiple external stimuli, e.g., light, pH, electrical fields, and so on, can switch reversibly between two entirely opposite properties. This article utilizes hydrophobicity and hydrophilicity as an example to demonstrate the feasibility of the design strategy, which may also be extended to other properties, for example, conductor/insulator, p-type/n-type semiconductor, or ferromagnetism/anti-ferromagnetism, for the design of other BSMI materials in the future.

1. Introduction

Learning from Nature means taking ideas from Nature and developing novel functional materials based on these concepts, as has been the case for, e.g., bio-inorganic materials (biomineralization),[1] bioinspired, multiscale structured materials (chiral morphologies),[2] bio-nanomaterials (bio-nanoparticles),[3] hybrid organic/inorganic implant materials (bone-like composites),[4] and smart biomaterials.[5,6] These bioinspired, smart materials are attracting more and more interest because of their unique properties, which have paved the way to many real-world applications, e.g., biomimetic fins,[7] actively moving polymers,[8] neural memory devices,[9] smart micro-/nanocontainers for drug delivery,[10] various biosensors,[11–13] dual/multi-responsive materials.[14,15] Also, many of these smart materials have surfaces that dynamically alter their physicochemical properties in response to changes in their environmental conditions and a triggered control of interfacial properties at the solid/water interface can be found in ion channels,[13] directional surface motions,[16] and bioinspired, smart surfaces with controllable wettability and adhesion.[17,18] The self-cleaning effect of lotus leaves,[19] the anisotropic de-wetting behavior of rice leaves,[20] the super-hydrophobic forces exerted by a water strider's leg,[21] the attachment mechanism of geckos,[22] and many other natural phenomena are all related to unique micro- and nanostructures on surfaces.[23–28] The creation of such complex functionalities in bioinspired materials depends on well-ordered multiscale structures. Here, we present a strategy for the design of bioinspired, smart, multiscale, interfacial (BSMI) materials based on this concept.

This review is organized into five sections. The first section gives a brief introduction to BSMI materials, while the second section summarizes the basic guidelines for their preparation. The third section provides a comprehensive overview of synthetic routes to four different types of BSMI materials: bioinspired functional, multifunctional, simple responsive, and smart interfacial materials. Lastly, an overview of potential applications of BSMI materials is followed by an outlook for future methods for the fabrication of BSMI materials.

2. Design of BSMI Materials

Smart materials reversibly response to both internal and external, environmental stimuli.[29,30] BSMI materials focus on

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interfacial response systems. As shown in Figure 1 we suggest five principles for the design of these materials: i) Selection of a unique property found in biology, which can serve as ‘‘bio’’–inspiration; ii) Understanding of the correlation between multiscale structure and macroscopic properties, because the correlation between the physico-chemical properties of a biological system and its multiscale structure is crucial for the design process of BSMI materials later on; iii) Design and synthesis of suitable target molecules, since selecting appropriate molecules (key building) is important for realizing the desired response properties; iv) Design of a two-way response using bistable states, given that cooperative response processes in biological systems change between bistable states based on multiple weak interactions, which are reversible; v) Construction of a binary cooperative complementary interface: in order to control the physical and chemical properties, these properties in bistable states should be different or may as well be totally opposite. While there are many mutually compensating properties, e.g., hydrophilic/hydrophobic; conductive/insulating, convex/concave, p-type/n-type,

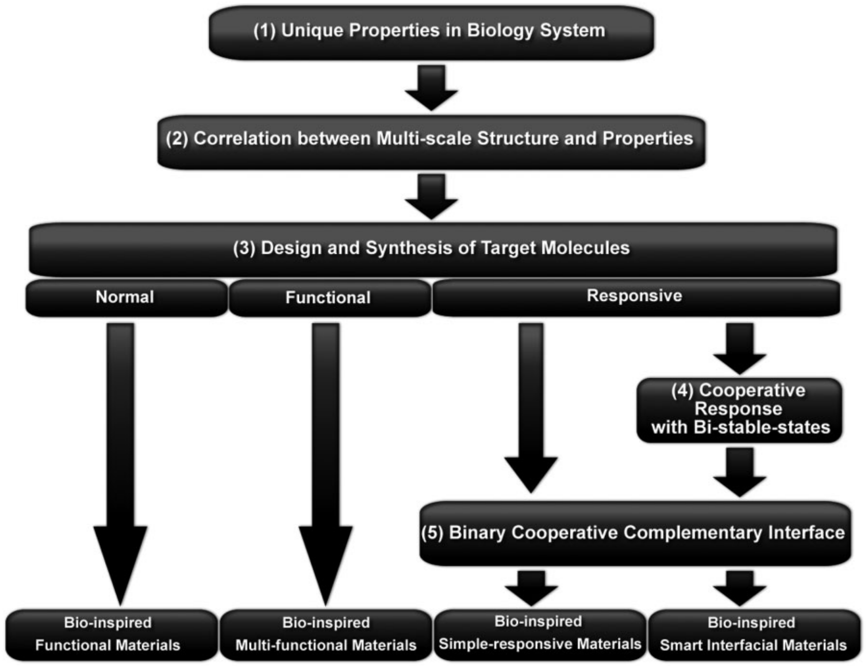

Figure 1. Schematic of the design process (learning from nature). Four design routes lead to four types of materials: bio-inspired functional materials; bio-inspired multifunctional materials; bio-inspired, simple-responsive materials; and bio-inspired, smart, interfacial materials according. The design process contains five principles. The first and second route each contain three principles, the third contains four, and the forth contains all five principles.

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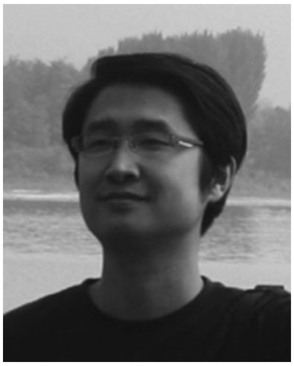

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oxidizing/reducing, ferromagnetic/anti-ferromagnetic, and so on, this paper only demonstrates the feasibility of our strategy using the concept of hydrophobicity/ hydrophilicity.

The selection of different principles when designing a material, that is following different routes during the design process, will create different materials. Hence, the four routes depicted in Figure 1 lead to different types of bio-inspired materials. The following sections will discuss each principle (Section 2) and review selected examples and routes of design processes (Section 3).

2.1. Unique Properties in Biological Systems

Selecting unique properties in biological systems and using them as bio-inspiration is the first step in learning from nature. Many scientific questions can be deduced from nature's smart responses to external factors. In general, biological systems are organic-inorganic hybrid composite materials which respond to external stimuli, e.g., smell, vision, hearing are responses to scent,[31] light,[32] and sound,[33] respectively, but these biological response systems are too complicated to be imitated directly. However, recently some less complex, but nonetheless special features in biology received intense attention (Fig. 2), such as, the self-cleaning effect of lotus leaves and duck feathers,[34,35] the non-fogging, super-hydrophobic compound eyes of mosquitoes,[36] the locomotion of geckos and octopuses via highly adhesive feet and suckers,[37,38] the non-wetting phenomenon of water striders walking on water,[39] the color of peacock feathers, butterfly wings, and beetle shells which is caused by a periodic microstructure,[40–42] the special nanostructures causing anti-reflectivity in cicada's wings and moth's compound eyes,[43,44] and lastly the special photonic reflectivity of sponge spurs due to their unique microstructure.[45] All these features are suitable for bio-inspiration.

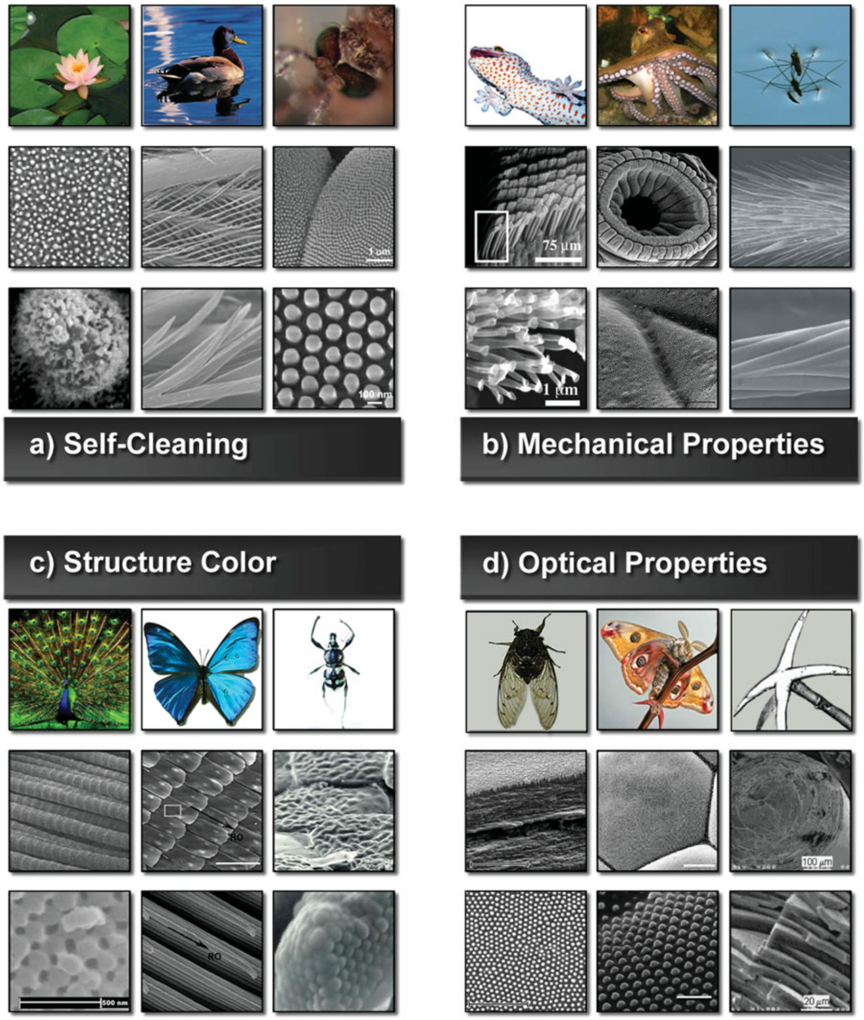

Figure 2. Multiscale structure in biology. Four types of interesting biological properties can be found in nature: a) self-cleaning properties: lotus leaf, duck feather, and mosquitos eye (from left to right), b) mechanical properties: gecko feet, octopus suckers, and water strider, c) color through structure: peacock feather, butterfly wings, and beetle shells, and d) optical properties: cicada wings, moth compound eyes, and sponge spur. In each case the first row shows a photograph of the biological feature, while the second and third row show scanning electron microscopy (SEM) images of corresponding micro- and nanometer-scale structures.

2.2. Correlation between Multiscale Structure and Property

Interestingly, many unique properties are related to special micro- and nanostructures (second and third row in Fig. 2) and understanding the correlation between the unique properties of a biological system and its micro- and nanometer-scale structure is critical for the fabrication of novel materials.

In the case of the "lotus effect", the phenomenon of superhydrophobicity observed in lotus leaves and duck feathers,[34,35] the original hypothesis was that both high contact angle (superhydrophobicity) and low sliding angle (low adhesion) were a result of surface roughness caused by micrometer-scale papillae and epicuticular wax. More recently however, the discovery of novel micro- and nanometer-scale hierarchical structures on the surfaces of lotus leaves, i.e., branch-like nanostructures on top of the micropapillae, let to the proposal that these hierarchical structures might be the reason for the unique properties observed. The combination of special structure and corresponding chemical composition leads to the unique properties observed in the lotus leaves, which is also the case for many of the following examples.

Researchers proposed that micro- and nanometer-scale hierarchical structures on biological surfaces, as exemplified by the scanning electron microscopy (SEM) images in Figure 2a (second and third row), can cause special phenomena such as the self-cleaning effect of lotus leaves and the anti-fogging properties of the compound eyes of mosquitoes.[36]

Geckos are known for their excellent ability to climb walls and run on ceilings (highly adhesive ''gecko'' feet),[37] and octopuses for their ability to anchor their body to the substratum and hold their prey (octopus suckers).[38] Meanwhile, water striders stand effortlessly and walk quickly on water due to their non-wetting legs. Figure 2b shows oriented, micrometer-scale, needle- shaped setae on the legs of water striders,[39] which are considered to be the origin of their superhydrophobicity.

The color of the feathers of a peacock, the wings of a butterfly, or the shell of a beetle,[40–42] is caused by microstructures that exhibit periodic variations in dielectric constant in one, two, or three dimensions (SEM images in Fig. 2c), with the period being in the order of the wavelength of the corresponding color. Color through structure is can be found in a significant number of animals, particularly those living in weakly lit environments, and in cases where the synthesis of a particular pigment is biochemically too expensive, e.g., green in beetles.[46]

Nanostructures found in the wings of cicadas and the compound eyes of moths (SEM images in Fig. 2d) can minimize reflectivity over a broad range of angles and frequencies,[43,44] through gradually matching the optical impedance of one medium with its neighbor across the interface. This is achieved through the integration of arrays of tapered elements, so called nipple arrays, into the boundary. Such nipple arrays are commonly found on arthropodal ommatidial surfaces and are currently the subject of considerable research activities. Likewise, the special photonic reflectivity of sponge spurs is ascribed to unique microstructure as well.[45]

In summary, many unique properties found in nature can be attributed to hierarchical structures. The practical realization of complex functionalities in bio-inspired materials depends on well-ordered, multiscale structures (micro- and macrostructures) produced by various physical and chemical methods, and is a crucial point in the design of novel BSMI materials. Therefore, learning from nature, grasping underlying algorithms, and applying them to artificial processes is the path pursued by many scientists.[47] Based on the correlation between property and multiscale structure of a biological system, artificial materials with similar or novel properties can be designed.

2.3. Design and Synthesis of Target Molecules

Apart from the multiscale structure, the design and synthesis of suitable target molecules is another important principle in the design of novel BSMI materials. Target molecules are required to be functional or be responsive to external stimuli with the capability to change their conformational structure and/or properties upon being exposed to an external stimulus. External stimuli can be classified into two types: physical and chemical stimuli. While the former includes light, electricity, magnetic fields, heat, and stress, amongst many others, the latter includes acids/bases, oxidizing/reducing agents, electrochemical forces, etc. The interest in target molecules has increased exponentially recently due to their promising potential. Figure 3 lists some of the many smart molecules described in the literature, i.e., thermo-, glucose-, pH-, electricity- or photo-responsive molecules.[48–53] If polarity, conformation, functional group of an interfacial molecule change, the physical properties of the stimuli responsive molecules change accordingly.

In summary, there are many functional and responsive molecules that are excellent building blocks for the fabrication of smart materials. Depending on the design, the synthesis, and the combination of the building blocks, different functional, single responsive and even dual/multiresponsive materials are possible. Some examples are listed in Section 3.

2.4. Two-way Responses via Bistable States

Although the conformation or orientation of a responsive molecule can change under external stimuli, this response on a molecular level is only the primary response in a biological system. The response process in biological systems is based on multi-weak-interactions, which are entirely reversible. In fact, biological systems at all levels of organization respond to external stimuli via multi-weak-interactions that act as reversible switches between cooperative bistable (multistable) states.

A very typical examples is the multi-weak-interaction among hemoglobin, oxygen, and carbon dioxide (Fig. 4).[54] There are two major conformations (bistable states) of hemoglobin, *R* state and *T* state, which induce two types of multi-weak-interaction between hemoglobin and oxygen. In the *T* state hemoglobin and oxygen are loosely bound, which results in the release of O_2 to organs and tissues, while hemoglobin in the *R* state and oxygen bind together strongly, which facilitates O_2 uptake in the lungs. These enthalpy-driven processes of O_2 uptake and release depend on the switch in multi-weak-interaction (hydrogen bonding) between the two cooperative bistable states of hemoglobin (*T* state and *R* state) and oxygen, which is a fully reversible process.

Designing entirely reversible response systems with cooperative multi-weak-interactions is another crucial point in the design of novel BSMI materials. Switch processes between cooperative multi-weak-interactions can either be entropy- or enthalpy-driven, whereby most switch processes in nature are driven by enthalpy, like the reversible, pH-responsive i-motif

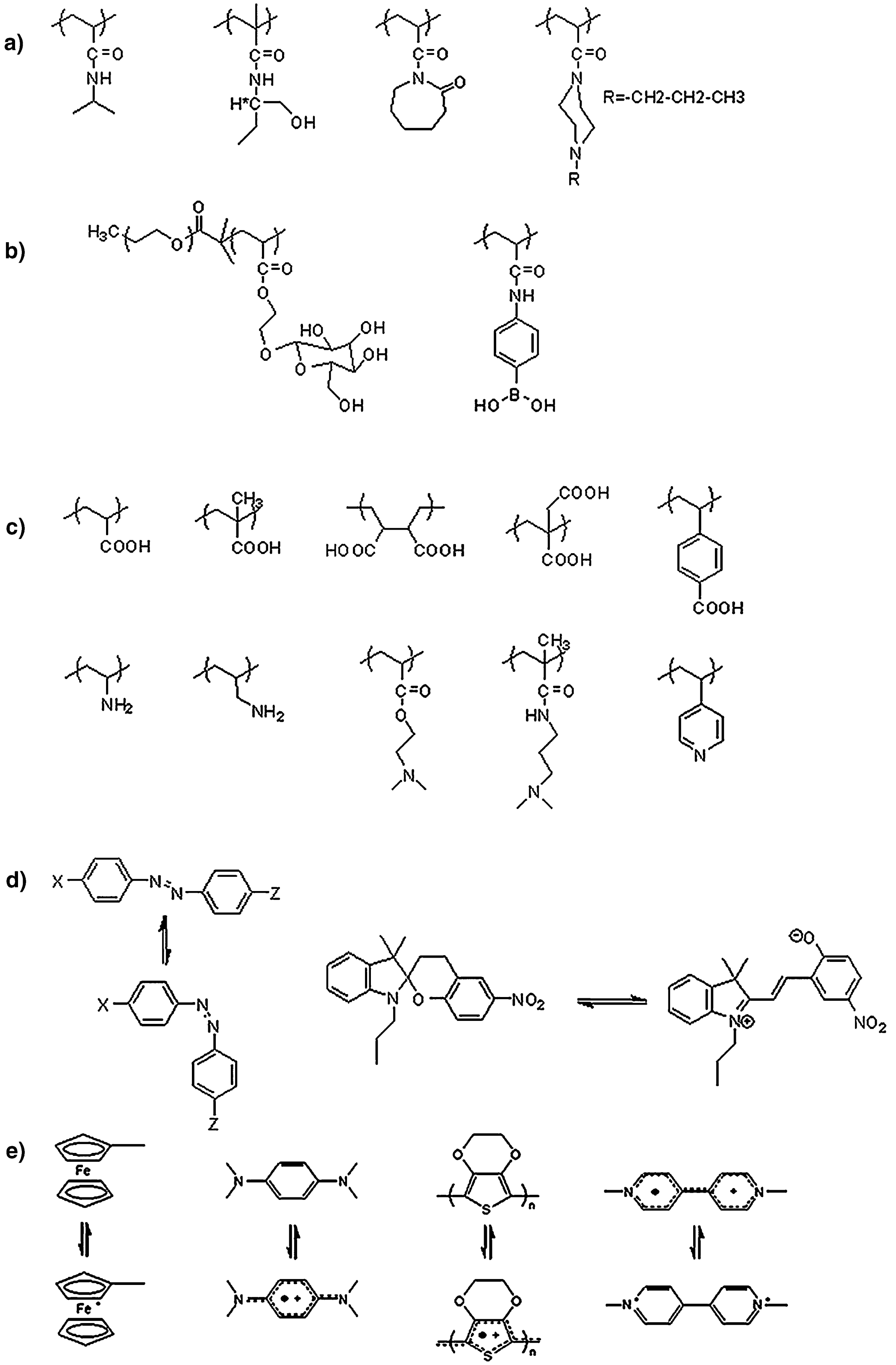

Figure 3. Typical stimuli-responsive molecules. a) thermo-, b) glucose-, c) pH-, d) electro-, and e) photo-responsive molecules.

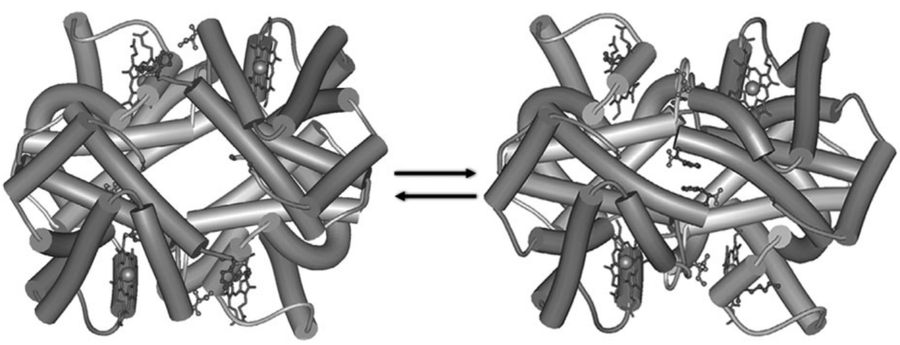

Figure 4. The $T \leftrightarrow R$ transition of deoxyhemoglobin. Reproduced with permission from [54]. Copyright 2001 W. H. Freeman & Co.

DNA conformation change for example.[55] Section 3 details some of these processes.

2.5. Binary Cooperative Complementary Interfaces

The purpose of constructing a cooperative response with bistable states is to control the physical and chemical properties. Therefore, the physical or chemical properties of the bistable states should be different or even complementary to each other. Figure 5 shows some physical and chemical properties that complement each other, e.g., hydrophilic and hydrophobic, conducting and insulating, convex and concave, p-type and n-type semiconductors, oxidizing and reducing, and ferromagnetic and antiferromagnetic behaviour. Recently, the novel concept of binary cooperative complementary nanometer-scale interfacial materials was proposed, i.e., materials that exhibit two complementary properties on the nanometer-scale and can switch reversibly between both properties on the "macroscale" under certain conditions.[56] Some recent results,[57–61] indicate that this concept is useful for the design of novel interfacial materials. Under certain conditions, these interfaces exhibit unexpected properties, providing a huge potential to be explored theoretically and many potential novel applications. Hydrophilicity and hydrophobicity are the two opposite extremes in wettability of a surface and artificial switches between hydrophilic and hydrophobic or even superhydrophilic and superhydrophobic that can be triggered by external stimuli, such as temperature, pH, light, etc.,[62–66] are excellent examples of BSMI materials.

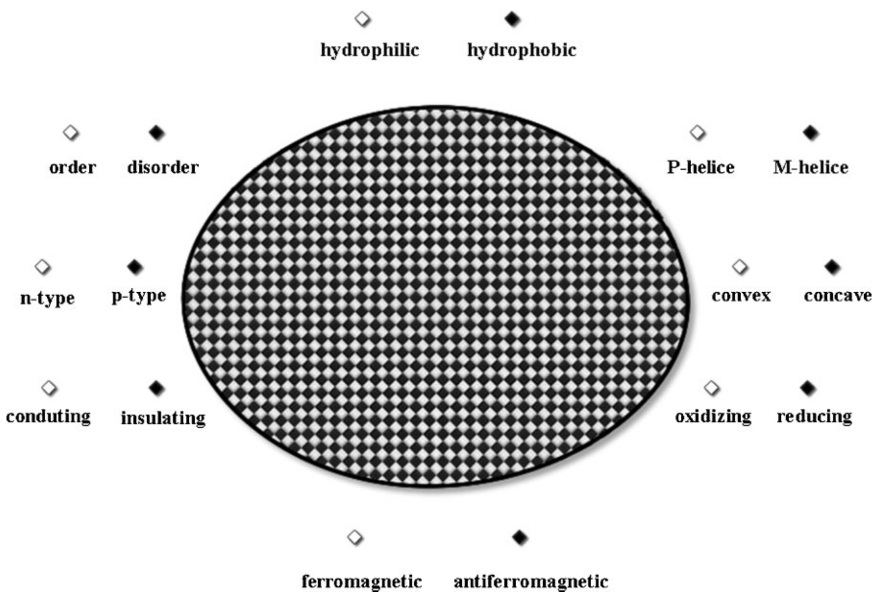

Figure 5. Possibilities for binary cooperative complementary nanometer-scale interfacial materials. Nanostructures with mutually complementary properties are presented by the squares in black and white. The motivation for the development of bio-inspired, multiscale, interfacial materials is the desire to create unique macroscopic functional properties. By applying the binary coordinating complementary concept to a solid surface on multiple length scales, nanostructures with mutually compensating properties were expected to be generated, e.g., hydrophilic/hydrophobic, conducting/insulating, convex/concave, p-type/n-type, oxidizing/reducing, ferromagnetic/antiferromagnetic, and so on. Reproduced with permission from [56]. Copyright 2000 Int. Union Pure Applied Chemistry.

3. Examples of BSMI Materials Design

Taking the lotus leaf as an example, its superhydrophobic and self-cleaning properties can serve as bio-inspiration. A great number of research focuses on the correlation between microstructure and macroscale property, and novel findings of micro- and nanometer-scale hierarchical structures on the surface of the lotus leaf, i.e., branch-like nanostructures on top of the micropapillae, enable us to explain such unique properties.[34] Since then, a number of researches on superhydrophobic surfaces were motivated by the aim to mimic nature and a lot of effort was put into the development of various artificial superhydrophobic surfaces.[67–71] Generally, surfaces with a static contact angle (CA) higher than 150° are defined as superhydrophobic surfaces. As shown in Figure 6, six different CA states and hystereses are possible for superhydrophobic surfaces: a) Wenzel's state (water droplets pin the surface in a wet-contact mode), b) Cassie's super-

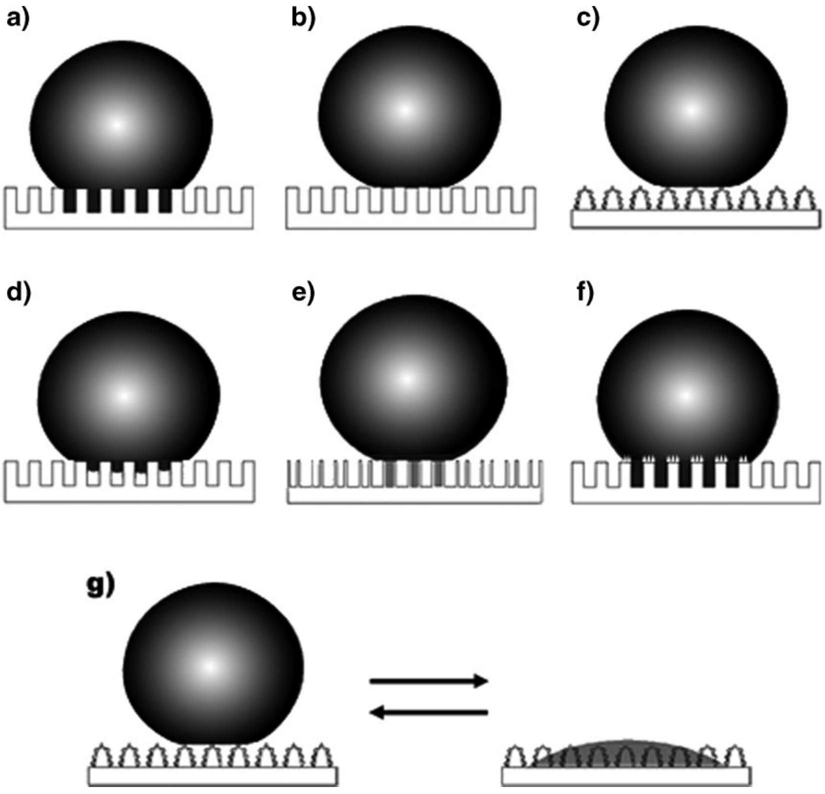

Figure 6. a–e) Different states of superhydrophobic surfaces. a) Wenzel's state, b) Cassie's state, c) the ''Lotus'' state (a special case of the Cassie superhydrophobic state), d) the transitional superhydrophobic state between Wenzel's and Cassie's states, and e) the ''Gecko'' state (e.g., of a PS nanotube surface). f) Cassie's impregnating wetting state. Gray shaded areas represent sealed air, whereas the other air pockets are continuous with the atmosphere (open state). g) Surface roughness increases wettability. Reproduced from [72].

hydrophobic state (water droplets adopt a non-wet-contact mode), c) ''Lotus'' state (special case of Cassie's superhydrophobic state, high CA and very small CA hysteresis), d) transitional superhydrophobic state between Wenzel's and Cassie's state (most practical samples, includes certain sliding angle), e) ''Gecko'' state (high CA and adhesion), and f) Cassie impregnating wetting state.[72,73]

Another good example are the superhydrophobic wings of a butterfly which exhibit directional adhesion (Fig. 7).[41] Droplets easily roll off the surface of the wings in radial outward (RO) direction from the central axis of the body, but are pinned tightly against the surface in the opposite direction. Interestingly, these two distinct states are controlled by the position of the wings (downwards or upwards) and the direction of the airflow across the surface (in or against RO direction). Research showed that this results from the directional arrangement of flexible nanotips on overlapping ridgid nanostrips and microscales at the one-dimensional level. Two distinct contact modes of water droplets and orientation-tunable microstructure are possible, thus providing two different adhesive forces. The arrangement and orientation of a micro/nanostructure can control different states of superhydrophobicity.

Additionally, roughness is also believed to alter wettability. A flat substrate with a CA higher than 65° becomes superhydrophobic when the roughness increases; and if the CA is lower than 65° the substrate becomes superhydrophilic with increasing roughness. The 65° CA is strongly related to the boundary between hydrophobic and hydrophilic, which was recently defined by surface tension measurements.[74] A certain surface roughness is necessary to obtain superhydrophilic and superhydrophobic surfaces, which can be derived theoretically from Wenzel's,[75] and Cassie-Baxter's law (Fig. 6g).[76] Together, these results give us an opportunity to fabricate surfaces that are switchable between superhydrophobicity and superhydrophilicity by combining surface roughness with chemical composition (examples in section 3.4.).

Again considering the lotus leaf, if hydrophilic or amphiphilic molecules were bound to a lotus-like superhydrophobic surface combining hydrophobicity and hydrophilicity on one and the same surface, then the lotus-like surface would become a responsive, switchable surface that utilizes the transitional Wenzel/Cassie superhydrophobic state. As for the wings of a butterfly, if low adhesion molecules and a ''Gecko'' state surface were combined then high and low adhesion could be realized with one material.

The following section focusses on bio-inspired materials with two basic features: special wettability and smart surfaces that respond to external stimuli. Based on the fundamental wetting states causing hydrophobicity/hydrophilicity, oleophobicity/oleophilicity, and high adhesion/low adhesion, any other type of surface function can be obtained by simple combination of any two aspects. So can for example for a solid substrate that exhibits micro-/ nanostructures as well as a very high surface free energy superhydrophilicity and superoleophilicity co-exist. The same is possible for rough surfaces with very low surface free energies. In following the routes given in Figure 1 smart materials which respond to external stimuli with opposite properties (i.e., bistable states) can be fabricated. Examples of all four types of bio-inspired materials corresponding to the four routes mentioned are given hereafter.

3.1. Bio-Inspired Functional Materials

3.1.1. Superhydrophobic Surfaces

Research in superhydrophobic surfaces originates from the lotus effect, but has since been extended to new surface materials with self-cleaning properties, whereby the interplay

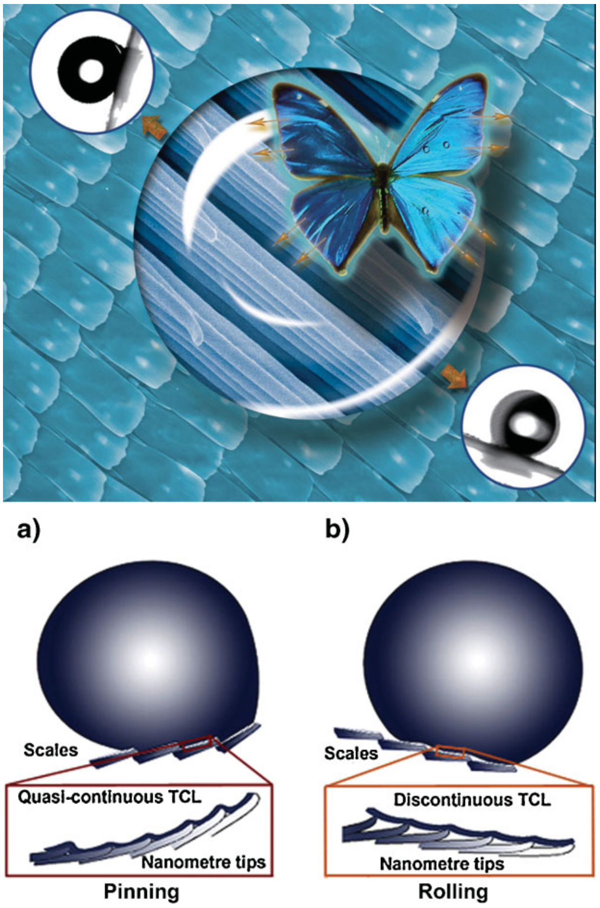

Figure 7. Directional adhesion of water on superhydrophobic *Morpho aega* (butterfly) wings. The proposed model for the mechanism depends on the direction of the airflow (in and against radial outward direction) and the position of the wing. a) If the wing is tilted upward, the flexible nanotips on the nanostrips and microscales take a close arrangement so that the droplet presents the "wet" contact to the nanostrips and forms a quasi-continuous TCL (three-phase contact line), which pins it to the surface. b) If the wing is tilted down, the nanotips on the nanostrips and microscales separate from each other so that the water droplet not only presents a 'composite' contact with the top of the nanostrips and a 'dry' contact with the air pocket trapped in the nano-grooves, but also forms an extremely discontinuous TCL, which both make it easy for the water droplet to roll off the surface. Reproduced with permission from [41]. Copyright 2007 Royal Society of Chemistry.

between surface roughness and low-surface-energy coating leads to their superhydrophobicity. Different chemical and physical methods for the fabrication of rough surfaces and subsequent application of low-surface-energy coatings on these rough surfaces have been explored, e.g., lithography,[77] sublimation,[78] plasma techniques,[79] self-assembled monolayers,[80] electrochemical methods,[81] electrohydrodynamic/electrospinning techniques,[82] and many more. Electrohydrodynamic techniques proved to be effective methods for the preparation of lotus-leaf-like porous microsphere/nanofiber composite films. Via this simple method a cheap industrial polymer affords superhydrophobicity without any further modification.[82] porous microspheres (Fig. 8) contribute to the superhydrophobicity by increasing the surface roughness, while nanofibers interweave to form a 3D network and reinforce the composite film that is surprisingly similar to a lotus leaf. Besides, for sublimable, pore-forming materials sublimation can be employed to produce rough surfaces. So is for example a surface roughness created on boehmite and silica films by simple sublimation of aluminum acetylacetonate during calcination, and subsequent coating with fluoroalkylsilane yields transparent superhydrophobic films of these materials.[83] Likewise, transparent, photocatalytic, superhydrophobic thin films are prepared by utilizing TiO_2 as sublimation material and subsequent coating with fluoroalkylsilane.[79]

Plasma enhanced chemical vapor deposition (PECVD) is a technique that produces perfectly aligned and untangled carbon nanotubes with controllable height and diameter. Superhydrophobic surfaces have been created using the intrinsic nanoscale roughness of a vertically aligned carbon nanotube forest in conjunction with a hydrophobic PTFE coating.[84] Microwave plasma enhanced CVD using organosilicon compounds and Ar gas at low temperatures has also been shown to yield ultrawater-repellent films.[85]

Nanostructured graphitelike carbon films can be prepared through a simple pyrolysis method and as-prepared films are superhydrophobic but not only for pure water but also corrosive liquids, such as acidic and basic solutions. This is an example of superhydrophobicity over the entire range of pH values which might open up new perspectives in the preparion of novel nanometer-scale, interfacial materials.[86] Even an inherently amphiphilic molecule (i.e., PVA) can be used to fabricate superhydrophobic surfaces since a re-orientation of PVA molecules occurs when they are confined to a nanosized space. This causes the hydrophobic groups to locate at the rough surface and the surface free energy decreases. This is a good example for amphiphilic materials being used to prepare superhydrophobic surface and validates Herminghaus' hypothesis that a super water-repellent surface can be constructed from a hydrophilic material.[87]

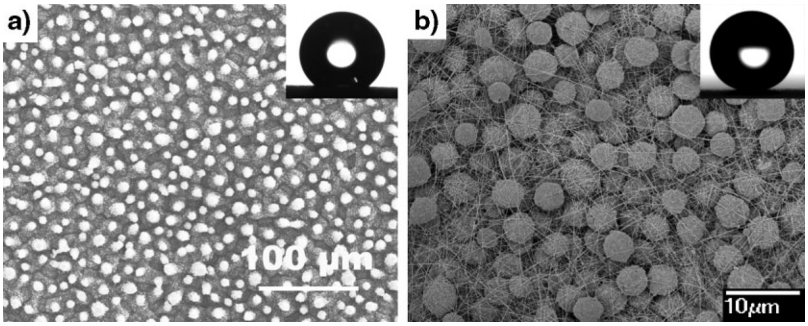

Figure 8. SEM images of a) a lotus leaf, and b) lotus-like surfaces fabricated by electrohydrodynamic techniques. Insets show water droplets on the respective surfaces. Reproduced from [20,82].

However, not only the surfaces but also the various edge effects on the outflow behaviors of water have been investigated to solve the troublesome problem of liquid outflow (spillage) at container edges that frequently brings about great inconvenience in daily lives.[88] A simple method of pressing a drop over the edges of a conical frustum was adopted to explore the stability of suspended drops around the edges. It was found that geometric morphology, surface microstructure, and molecule characteristics play an important role in controlling the stability. This result is potentially very helpful for innovative designs of tubes and bottles, e.g., to solve the problem of liquid outflow at the edges. The material design could be accomplished by carefully balancing micro-/nanostructure and surface free energy. However, these materials limited applications due to their single function.

3.1.2. Highly Adhesive Surfaces

Inspired by butterfly wings and gecko feet some multiscale structured and highly adhesive surfaces were fabricated. One example are superhydrophobic aligned polystyrene nanotube films which are composed of more than one million aligned nanotubes per squaremillimeter and are highly adhesive, similarly to the feet of a gecko (Fig. 9a). Interestingly, this layer can hold water droplets through strong adhesive forces, even when the layer is turned upside down and could therefore be used to transfer a water droplet from a superhydrophobic surface to a hydrophilic one. As-prepared films are not only superhydrophobic but also highly adhesive.[89]

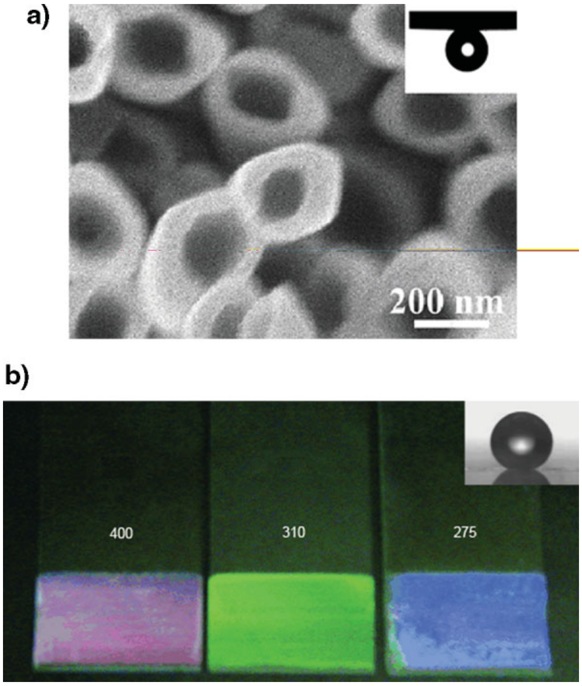

Figure 9. a) SEM image of a highly adhesive surface built from superhydrophic aligned polystyrene nanotubes. Inset shows the water droplets are strongly adhered to the surface even when turned upside down. b) Photograph of superhydrophobic surfaces exhibiting color through structure. Inset: water droplet on inverse-opal coated glass substrate modified with a fluoroalkylsilane. Reproduced from [89,92].

Another example are vertically aligned (VA) single wall carbon nanotube (SWNT) arrays produced via a combination of PECVD and fast heating process which have the highest macroscopic adhesive force among all synthetic and natural gecko feet. Furthermore, dry adhesives based on these vertically aligned SWNT exhibit reversible semiconducting behavior under load as well as excellent thermal resistance due to the unique thermal and electric properties intrinsic to SWNT.[90] These unusual multifunctionalities makes VA-SWNT dry adhesives very attractive for many diverse applications ranging from self-sensing over packaging to smart electronics with patterned or non-patterned electrical/thermal management capabilities. A synthetic adaptation of the fibrillar adhesion surfaces that are commonly found in nature has also been reported. The structure consisted of protruding fibrils topped with a thin plate and showed an enhancement in adhesion energy of up to a factor of 9 over a flat control. Additionally, this structure solved the problem of robustness of previous structure mimics and showed desirable contact properties (i.e., a large surface area and a highly compliant structure). The fibrillar geometry enhances adhesion because of its ability to trap interfacial cracks in highly compliant contact regimes between successive fibril detachments. This particular research also showed that the fibrillar geometry tends to pin the contact upon retraction and fails incrementally in a more stable way than does the flat control.

In summary, the key to control surface wettability and adhesion is to manipulate the chemical composition or topological nature, or both.

3.2. Bio-Inspired Multifunctional Materials

While common functional materials self-limit their field of application due to their simplicity, bio-inspired multifunctional materials have broader applications due to the fact that they were synthesized to have multiple functionalities. Functional materials include materials with important applications in modern and future technologies, such as conductive,[91] structure color,[92] and superoleophobic/superhydrophobic materials.[93] Some functional materials were fabricated according to the following three principles: i) Unique property in a biological system, ii) Correlation between multiscale structure and property, iii) Design and synthesis of target molecules.

For instance, conductive but at the same time superhydrophobic rambutan-like polyaniline hollow spheres were prepared via a self-assembly process of polyaniline in the presence of perfluorooctane sulfonic acid as the dopant.[91] The conductive rambutan-like hollow spheres exhibited a large specific surface area and superhydrophobic properties and may therefore find potential applications in biosensors and drug delivery. As shown in Figure 9b, uniform inverse opal films can be formed on nanostructured surfaces,[92] thereby achieving both structural color and superhydrophobicity simultaneously. Such films are anticipated to become the new generation of decorative materials. Additionally, the surface of the inverse opal obtained via this method is composed of 2D ordered nanodots, which may lead to a new approach on the fabrication of a quantum dot arrays. Further applications in the fields of nanomaterials, optical devices, and biology are anticipated.

Recently, a simple method for the fabrication of highly stable superamphiphobic surfaces (high CAs for both water and oil) via direct self-organization of dandelion-like structures was reported. Low contact angle hystereses for water and oil endow the as-prepared superamphiphobic surface with an excellent self-cleaning property and both water and oil droplets run off the surface at small tilt angles. Thanks to these excellent water- and oil-repellent properties as well as long environmental stability of such surfaces this approach could offer an alternative to practical industry problems, e.g., self-cleaning of buildings and reduction of friction in the transportation of heavy oil.[93]

In summary, the key to control surface wettability and adhesion is to manipulate the chemical composition or topological nature, or both, and this includes some slightly different functional molecules than those used in section 3.1.

3.3. Bio-Inspired Simple-Responsive Materials

Comparing functional materials with responsive materials shows that latter ones are advanced materials due to their ability to respond to ambient stimuli. The route for constructing simple-responsive materials (route three in Fig. 1) includes four principles. In addition to those discussed earlier it includes bistable states, but it is a simple response process without multi-weak-interaction.

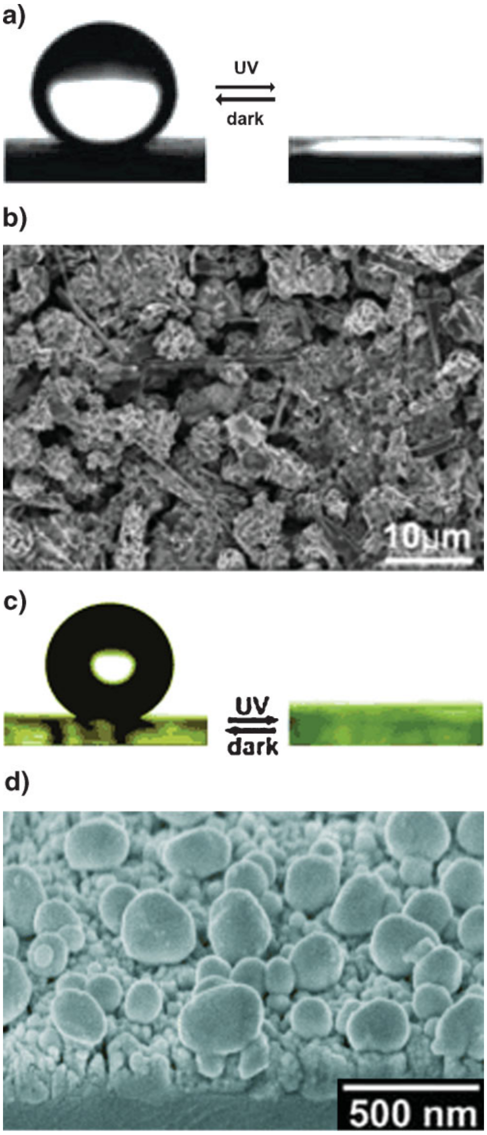

Figure 10. a) Water drop profiles for photo-responsive nanostructured V_2O_5 switching between superhydrophobicity and superhydrophilicity upon UV irradiation. b) SEM of the rose-garden-like nanostructure of the V_2O_5 substrate. Reproduced with permission from [97]. Copyright 2007 American Chemical Society. c) Water drop profiles for a photo-responsive switch between superhydrophobicity and superhydrophilicity of tungsten oxide film before (left) and after (right) ultraviolet irradiation. d) The morphology of the nanostructures resembles a pebble beach. Reproduced from [94b].

3.3.1. Photo-Responsive Surfaces

Some inorganic oxides always occupy paramount positions in many industrial applications because of their intrinsic advantages, e.g., good chemical and mechanical stability, low cost, and outstanding photoelectric properties. In recent years, the study of photoinducable and – controllable surface wettability has emerged as an exciting topic in surface science. As one class of photosensitive materials, inorganic semiconductor oxides such as WO_3, TiO_2, ZnO, SnO_2, V_2O_5, and Ga_2O_3 are famous for their capability of switching their surface chemical environment between two stable states (oxygen vacancies and hydroxyl groups). [94–97] Therefore, fabrication of micro-/nanometer-scale rough surfaces using these materials yields responsive surfaces which switch reversibily between superhydrophobicity and superhydrophilicity by simple alternating UV irradiation and dark storage (Fig. 10a). V_2O_5 rose-garden-like films that reversibly switched between superhydrophobicity and superhydrophilicity upon exposure to light and darkness were reported (Fig. 10b).[97] The superhydrophilicity of the surface upon exposure to UV light is closely related to the preferential adsorption of water on the photogenerated surface defect sites and the nanostructure of the surface with its sub-micrometer to micrometer scale apertures strongly enhances the wettability. On the one hand, when the film is hydrophobic, the rough surface increases the air/water interface,[75] on the other hand, when the film is hydrophilic (as a result of irradiation with ultraviolet light), water enters the microgrooves beneath the water drop.[98] In these two states, the surface roughness is the dominant factor that intensifies both hydrophobicity and hydrophilicity. This observation can be described theoretically by Wenzel's and Cassie-Baxter's laws which express the contact angle for a liquid droplet on a rough solid surface and explain how an increased surface roughness increases the wettability. The use of inorganic oxides in the fabrication of smart responsive surfaces would greatly extend their application to even more important fields. Photo-stimulative, dual-responsive tungsten oxide nanofilms can be prepared through a simple electrochemical deposition process. They show reversible conversion of wettability between superhydrophobicity and superhydrophilicity (Fig. 10c), and photochromism at the same time. The morphology of their nanostructures resembles a pebble beach (Fig. 10d). Interestingly, the as-prepared film turned yellowish-green (initially brown) upon UV irradiation and when this film was placed in the dark it turned brown again. Further studies revealed that the switching process involved reversible changes in tungsten oxidation state, oxygen vacancies, oxygen gas, and adsorbed water molecules.

Besides inorganic compounds, some organic compounds can also show the behavior of switchable wettability, and a facile route for finely controlling the wettability transition temperature of colloidal-crystal films from superhydrophilic to superhydrophobic was reported. The colloidal-crystal films were assembled from poly(styrene-*n*-butyl acrylate acrylic acid) amphiphilic latex spheres. This approach offers the flexibility of fabricating colloidal crystals with desired and tunable wettability, and can be further extended to other more general materials. Favored photoresponsive organic materials usually show a reversible photoinduced transformation between two states. For example, azobenzene, a typical photo responsive organic material, undergoes a reversible conformational transition between *cis* and *trans* isomers under ultraviolet and visible irradiation. These organic materials provide an abundant source for the fabrication of photo responsive surfaces with controllable wettability,[99] and other facile methods for the preparation of photoswitchable nanoporous multilayer films which reversibly change between two wettability states upon ultraviolet and visible irradiation have been reported, e.g., use of the photoswitchable agent, 7-[(trifluoro methoxy phenylazo) phenoxy] pentanoic acid.[65]

3.3.2. *Electro-Responsive Surfaces*

Recently, the use of electrical potentials as switches received special attention because it is a simple concept and conveniently controlled by electricity.[100–102] Lahann et al. constructed an electro-responsive, reversibly switching surface by depositing a low-density, carboxylate-terminated self-assembled monolayer on a gold surface.[100] Then an electrical potential was used to trigger a conformational transition of the monolayer which resulted in a switch in surface wettability. Upon application of an external electric potential to the gold substrate a reversible conformational transformation of the surface anchored mercapto chains between "bent" and "straight" states was caused through electrostatic effects between the ionized terminal groups and the charged gold substrate. Thus, either a hydrophobic or hydrophilic surface was established and reversibly switched by electrochemical driving forces. Accordingly, microchips prepared in a similar this way would be able to reversibly and selectively adsorb and release differently charged proteins upon electrical control.

3.3.3. *pH-Responsive Surfaces*

pH-responsive materials find application in many fields, e.g., drug delivery systems, enzyme immobilization, separation, chemo-mechanical systems, chemical valves, and sensors. Particularly, the design and the artificial control of the environmental pH stimuli are important in some cases.[103] Electrodeposition techniques were employed for the fabrication of micro-/nanostructured, rough gold composite surfaces and a self-assembly approache was pursued for the surface modification thereof by alternating monolayers. The resulting surface was superhydrophobic to acidic droplets of low pH and superhydrophilic for basic water droplets of high pH. When a rough gold substrate was modified with 2-(11-mercaptoundecanamido) benzoic acid a similar pH-response was observed. The pH-responsive wettability on such surfaces is caused by the reversible protonation and deprotonation of surface carboxylic acid groups.

3.3.4. *Stress-Responsive surfaces*

Usually, the wettability is controlled by reversible change of the chemical composition, but it has recently been recognized that the wettability of surfaces is governed by both chemical composition and surface structure. In this context, Han et al. reported a method to switch reversibly between superhydrophobicity and superhydrophilicity by biaxially extending and releasing an elastic polyamide film.[104] SEM image showed that the elastic film had a triangular net structure that was superhydrophobic, but was superhydrophilic when the film was biaxially extended in both directions. The switchable surface response if caused by both the surface tension of water and the average side chain length change of the triangular structure upon biaxial extension and release.

3.3.5. *The Movement of Droplets*

Despite the enormous interest in switching between wetting and dewetting behavior of surfaces, the movement of droplets on surfaces has also been studied. For instance, Ichimura et al. reported the photo-driven macroscopic movement of a liquid droplet on a photoresponsive solid surface of azobenzene.[105] They assembled a photoresponsive monolayer surface using an azobenzene derivative. Asymmetrical photoirradiation can cause a gradient in surface free energy because of the photoisomerization of surface azobenzenes, and if a liquid droplet several millimeters in diameter is placed on the modified surface, it will be forced to undergo directional motion. UV irradiation results in polar *cis*-azobenzene groups at the terminal positions, thereby increasing the surface free energy and hydrophilic nature of the surface, while photoirradiation with blue light causes *cis*-to-*trans* isomerization, which makes the surface more hydrophobic. Therefore, an imbalance in contact angle is generated between both edges of the droplet and the resulting gradient of surface free energy acts as driving force for the motion of the liquid. Thus, the motion of a droplet is readily controlled by varying the direction and steepness of the light intensity gradient.

In addition, magnetic fields can be used to control the movement of aqueous drops on non-patterned, superhydrophobic silicon nanowire surfaces.[106] The movement of droplets of aqueous and other biological fluids can be controlled by introducing magnetizable carbonyl iron microparticles into the liquid. Some key elements of operations such as movement, coalescence, and splitting of water and biological fluid drops, as well as electrochemical measurement of an analyte were demonstrated using this concept. The superhydrophobic surfaces were prepared using vapor-liquid-solid (VLS) growth systems followed by coating with perfluorinated hydrocarbon molecules. Observed movement of drops is due to the formation of particle chains under the influence of a magnetic field which press against the surface of the drop and overcome capillary and surface friction forces. By alternating the magnetic field the superhydrophobic surface was used for the reversible, oriented transport of superparamagnetic microliter-sized liquid droplets without loss of volume between alternating magnetic fields, which is of great significance for innovative designs of open, microfluidic devices.[107]

3.3.6. Bio-Inspired Surfaces with Switchable Adhesion

The combination of patterning technologies and responsive polymer materials has allowed us to create microstructured surfaces with switchable adhesion properties. Micropatterned surface designs are inspired by the attachment pads of many butterfly wings and gecko feet, which are known for their ability to strongly attach to and easily detach from almost any kind of surface.[22] As an additional feature beyond those of the natural systems, it was attempted to make the surface topography of artificial systems switchable between non-adhesive and adhesive state. Shape memory thermoplastic elastomers were used to fabricate micropatterned adhesive surfaces by soft molding of the material at the highest transition temperature,[108] which yielded arrays of vertical micropillars. Mechanical deformation of this topography at the second (lower) transition temperature followed upon cooling to room temperature and the deformed state was non-adhesive and the surface consisted of pillars in a tilted position. Reheating above the transition temperature resulted in a permanent switch from the temporarily non-adhesive state to an adhesive surface with at least a 200-fold increase in pull-off force. Applications of such systems in, e.g., pick-and-carry elements or medical tapes, can possibly impact on future technologies and devices.

Moreover, researchers attempted to capture the properties of adhesive gecko feet in synthetic mimics with nanometer-scale surface features similar to setae; however, maintaining adhesive performance over many cycles has been elusive so far and generally adhesion is greatly diminished upon full immersion in water. Another biologically inspired adhesive consisting of an array of nanofabricated polymer pillars coated with a thin layer of a synthetic polymer that mimics the wet adhesive proteins found in mussel holdfasts has been reported.[22] Wet adhesion of the nanostructured polymer pillar arrays increased nearly 15-fold when coated with the mussel-mimetic polymer. The system maintains its adhesive performance for over a thousand contact cycles in both dry and wet environments. Therefore, this hybrid adhesive, which combines the salient design elements of both gecko and mussel adhesives, should be useful for reversible attachment to a variety of surfaces in any environment.

All simple responsive surfaces have bistable states between they reversibly switch upon being exposed to external stimuli. However, these bistable states are not stabilized by multi-weak-interaction such as hydrogen bonding, are therefore called simple responsive. In the following some examples for response processes with multi-weak-interactions are discussed.

3.4. Bio-Inspired, Smart, Multiscale Interfacial Materials

By combing interface, structure, function, bistable states, and multi-weak-interaction single-responsive materials and even multi-responsive materials can be realized.

3.4.1. Single-Responsive interfaces

Some contributions to reversibly switching surfaces between superhydrophobicity and superhydrophilicity show excellent integration of all five design principles mentioned earlier. Here, some examples show how to design smart interfacial materials according to the fourth route in Figure 1.

3.4.1.1. Thermo-Responsive Interfaces: First of all, the self-cleaning effect of some plant leaves is of great interest for many practical applications (Fig. 11) and has been used as bio-inspiration for many researches on superhydrophobic fabrication methods and more recently smart material systems. Since the total opposite of hydrophobic is hydrophilic, surfaces have been designed that combine the mutually compensating properties of hydrophobicity and hydrophilicity.

The second step was to choose the stimuli responsive molecule. Poly(*N*-substituted acrylamide) (PNIPAAm) is the most popular temperature-responsive polymer because of its sharp phase transition in water at around 32 °C.[109] The NIPAAm segment can been designed to control the lower critical solution temperature (LCST) as well as the response kinetics at the molecular level. Thus, NIPAAm is a suitable target molecule for responsive films.

When PNIPAAm was grafted onto a flat silicon surfaces the thin film exhibited thermo-responsive switching between hydrophilicity and hydrophobicity. With increasing temperature the water CA increased about thirty degree. This effect can be explained by the competition between intermolecular

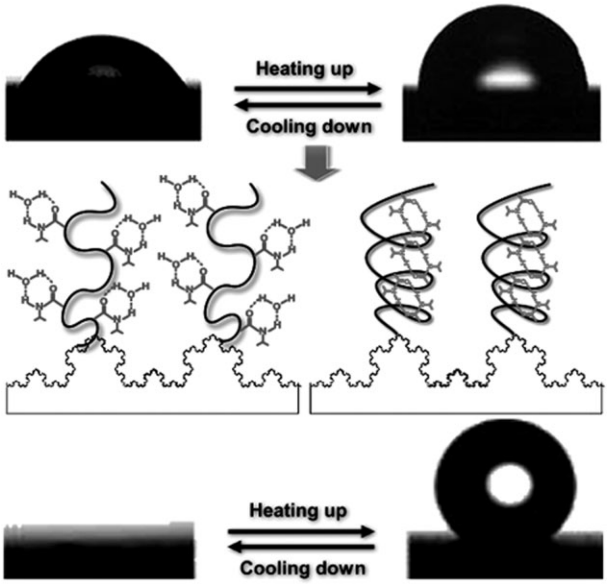

Figure 11. Fabrication of thermo-responsive interfacial materials. Reproduced from [109].

and intramolecular hydrogen bonding below and above the LCST.[110] At temperatures below the LCST the predominantly intermolecular hydrogen bonding contributes to the hydrophilicity of PNIPAAm films whereas at temperatures above the LCST increased intramolecular hydrogen bonding results in hydrophobic films. The switch between inter- and intramolecular hydrogen bonding involves the bistable states with multi-weak-interactions.

As for rough substrates with PNIPAAm modification, thermo-dependent experiments indicated that thermo-responsive wettability was greatly enhanced by surface roughness. This shows that thermo-responsive switching between superhydrophilicity and superhydropobicity can be realized by sufficient surface roughness of the substrate. Based on this study, Lopez et al. realized a superhydrophobic/superhydrophilic switch by modifying PNIPAAm brushes (thickness comparable to surface corrugation) on nanostructured, nanoporous anodic aluminum oxide surfaces.[111] Additionally, a novel rubber film, prepared by a simple mixing method, reportedly realizes a steep temperature dependence of the contact angle of water at the critical temperature of 41 °C. This rubber film showed a distinct switch of surface wettability between temperatures below 41 °C (hydrophilic) and temperatures above 41 °C (hydrophobic). The switching property is possibly controlled by the ratio of PNIPAAm to SBR, the method of preparation, and other factors. This technique can be applied for the control of surface wetting properties by temperature for various SBR-like rubber materials, and improve the performance thereof, e.g., the wet-brake performance of automobile tires on a rainy day.[112]

In addition to polymers, thermo-responsive cellulose nanolayers were prepared from methylcellulose (MC), which is known to have a unique LCST. Thiosemicarbazide (TSC) was selectively introduced into the reducing end groups of MC and the corresponding MC–TSC derivative chemisorbed on a Au substrate to give MC self-assembled monolayers (SAMs). The linear MC chains were stably bound onto the Au substrate, resulting in a MC-SAM with a thickness of approximately 15 nm and a root-mean-square-value below 1 nm.[113] The MC-SAM surface exhibited thermo-responsive wetting characteristics possibly caused by the solid-state phase transition of MC nanolayers due to inherent gelation of MC molecules in water. Such wetting behavior could be shown to be reversible following repeated heating and cooling cycles. MC-SAMs immersed in salt solution revealed lower phase transition temperatures, i.e., an increase in sodium chloride concentration from 0.0M to 1.0M brought about a dramatic decrease in the apparent phase transition temperature. Such controllable wetting properties of purposely designed MC nanolayers are expected to prompt a growing interest in the application of cellulose biopolymers at interfaces.

3.4.1.2. Solvent-Responsive Interfaces: Minko et al. reported the successful control of wettability by exposing a polymer surface to different solvents, even at comparatively large scales.[117] The heterogeneous binary polymer brushes, which were sensitive to toluene, ethanol, and water, consisted of an assembly of polymer chains of two incompatible polymers and their switching behavior was amplified by the texture of the material. As a result, the wettability of a fabric produced from the mixed brushes could be switched from complete superhydrophilic to superhydrophobic states. These solvent-sensitive surfaces find diverse applications such as reversible chemical patterning, smart sensors, and microfluidics.

3.4.2. Dual/Multi-Responsive Interfaces

Although many stimuli-responsive surfaces exhibiting reversible wettability have been fabricated, they are only responsive to one kind of external stimuli. For some

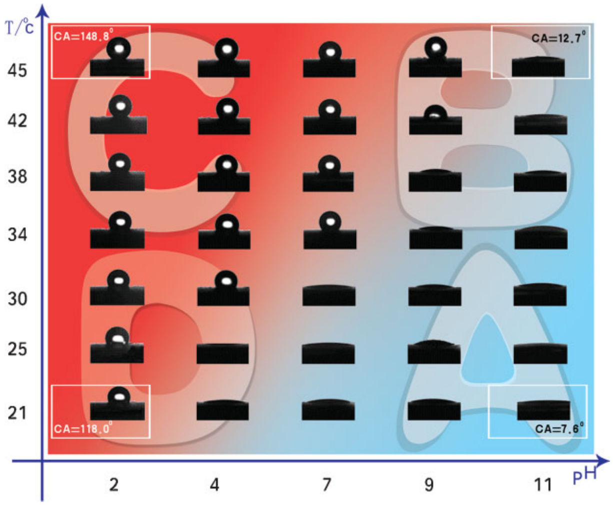

Figure 12. Upon variation of pH and/or temperature the contact angle of water and poly(NIPAAm-*co*-AAc) copolymer thin films changed. Reproduced from [62]

applications dual/multiple-responsive materials are required, e.g., when a drug needs to be delivered to a particular part of the body where temperature, pH, and glucose concentration differ from those found at other parts, then the carrier of the drug must be responsive to several stimuli at once, including temperature, pH, and glucose.

Based on above discussed single-responsive surfaces dual-stimuli-responsive surfaces that simultaneously exhibit temperature- and pH-sensitive wettability were prepared. The design process for these surfaces is similar to that of single-responsive ones, but requires two types of stimuli-responsive polymer. As shown in Figure 12 such surfaces were realized with poly(NIPAAm-*co*-AAc) copolymer thin films on rough silicon substrates. Reversible switching between superhydrophilicity and superhydrophobicity occurs in both a narrow temperature range of about 10 °C and a relatively broad pH range of 9. This behavior can mainly be attributed to reversible changes in H-bonding between the two polymer components, NIPAAm and AAc, and water. The wettability of the film depends on the competition between intermolecular and intramolecular hydrogen bonding. Furthermore, the LCST of these surfaces can be controlled by incorporation of hydrophobic or hydrophilic moieties. Adjustment of the LCST to a value close to body temperature is particularly important for drug delivery applications. Furthermore, the dual responsive poly(NIPAAm-*co*-AAc) hydrogels contain submicrometer sized cages which can be useful as drug carriers.[62] Recently, a superhydrophobic PANI-PAN coaxial nanofiber was fabricated through combination of electrospinning and polymerization. This fiber exhibited a chemically-responsive surface wettability that was readily controlled by adjusting the pH and/or the redox properties of a probe solution,[115] with the pH-responsive, reversible conversion between superhydrophobicity and superhydrophilicity being achieved very quickly. The controllable surface wettability of such dual-responsive PANI-PAN coaxial nanofibers suggests many new applications in the fields of biological separation systems, cell culture, sensors, etc. In the future, this synthesis strategy may be a straightforward method to control the wettability of smart surfaces using low-cost, functional polymers.

Based on this study, multi-stimuli-responsive surfaces, which reversibly switch between superhydrophilicity and superhydrophobicity in response to glucose, temperature, and pH, were fabricated.[63] Temperature- and pH sensitive PNIPAAm was included in the surface as well as glucose-sensitive poly(acrylamido phenylboronic acid) (PPBA), which forms stable complexes with glucose via its borate groups. Poly(NIPAAM-*co*-PBA) copolymer films were grafted onto flat and rough silicon substrates using surface initiated atomic transfer radical polymerization (ATRP). As shown in Figure 13, the surfaces reversibly changed between superhydrophilicity and superhydrophobicity under all three external stimuli: temperature, pH, and glucose. Poly(NIPAAm-*co*-PBA) grafted hollow microballs with porous shells may be excellent candidates for novel noninvasive glucose sensors and insulin self-delivering systems for instance, which would decrease the frequency of insulin injections for diabetic patients.

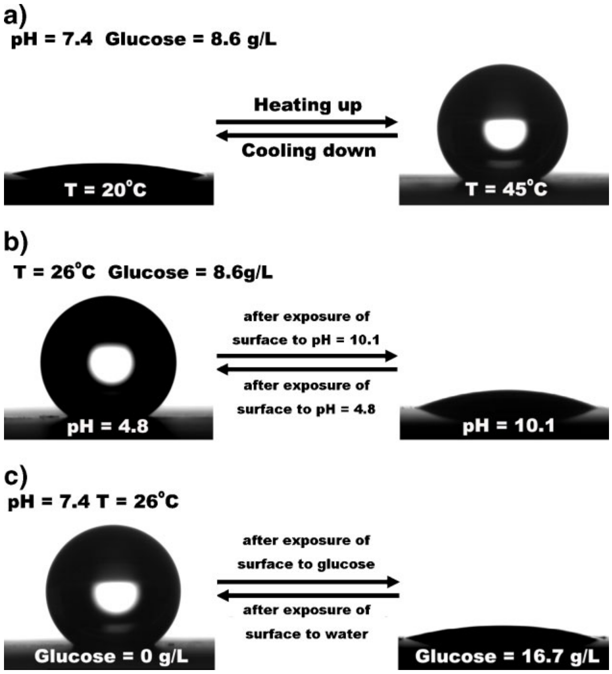

Figure 13. The contact angle (CA) between water and poly(NIPAAM-*co*-PBA) copolymer films on rough substrates changed with each of the three stimuli: temperature, pH, and glucose concentration. a) When pH and glucose concentration were fixed, the CA changed with temperature. b) When temperature and glucose concentration were fixed, the CA changed with pH. c) When pH and temperature were fixed, the CA changed with glucose concentration. Reproduced from [63].

The design of dual/multi-responsive surfaces is very simple according to the five design principles mentioned above. Only a change in target molecule (principle three) is required in the forth route in Figure 1 to obtain dual/multi-responsive surfaces instead of single-responsive films.

3.4.3. Enthalpy-Driven Switching of a Surface

Although many different smart surfaces have been described, so far nearly all of these switches in surface wettability are limited to entropy-driven processes, while enthalpy-driven switchable surfaces are not very well explored, even though various important life phenomena and molecular recognition behaviors are enthalpy-driven. Using the alanine helix as a model system to study the energetics of the interaction between water and helical peptide groups, which is probably a major factor in protein folding, it was found that the formation of the helix is an enthalpy-driven process.[116,117] Enthalpy-driven smart surfaces that switch between superhdrophilicity and superhydrophobicity were created using i-motif DNA strands (Fig. 14) and following route four of the design process.[55] This macroscopic surface phenomenon originates from the collaborative effects of surface microstructure and collective nanometer-scale motion of DNA

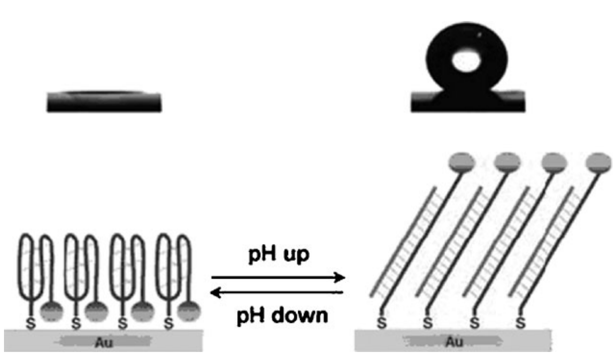

Figure 14. Intelligent, reversibly switchable surface driven by DNA nanodevices. At low pH the DNA adopts an i-motif conformation (state I) which gives way to a duplex structure (state II) when the pH is raised and the complementary strand is present. Lowering the pH reverses the process and converts state II back to state I. Reproduced from [55].

nanodevices. The DNA strands, modified with a fluoride containing hydrophobic group, were immobilized on a gold surface via gold-thiol bonds. In order to achieve better switching performance DNA strands X were pre-folded in phosphate buffered saline at low pH and then immobilized onto the Au surface where they formed a self-assembled monolayer of i-motif DNA. Under basic conditions and in the presence of complementary strands Y, their i-motif surface structure (state I) was converted to a duplex structure (state II). The original state of the DNA could then be recovered through the addition of acid. The transformations are enthalpy-driven processes and could provide models for cognitive biological behavior, i.e., short-term and long-term memory, as well as open new pathways for the design of intelligent surfaces.

Since switching between bistable states is vital for BSMI materials, the next question is whether this process is spontaneous or not. The Gibbs function can give an answer. If ΔG is negative, then a reaction or process has a natural tendency to shift spontaneously from reactants/reagents to products, but if ΔG is positive, then the opposite is the case and the reaction or process will not proceed spontaneously in this direction and the reverse reaction will be spontaneous.

DNA strands X were also integrated into single nanopores of polyethylene (PET) films. After the DNA was grafted onto the inner wall of the nanopore high- and low-conductance states were found within the artificial ion channel at high and low pH, respectively, corresponding to the different conformations of the "DNA motor". Many membrane proteins that form nanopore channels change their conformation between two or more distinct states, some of which allow the channels to transport certain ions or molecules, while others inhibit ionic or molecular transport altogether. Conformational transition between these states is usually referred to as gating.[118] Such enthalpy-driven nanogating devices may open unexpected opportunities in surface and biological science and will be of immense value to materials science.

4. Applications of Bio-Inspired, Multiscale, Interfacial Materials

Research on bio-inspired, interfacial materials is mainly driven by functional applications. Superhydrophobic surfaces are interesting because self-cleaning and nonstick properties of surfaces are prominent,[119] and desirable for many industrial and biological applications, e.g., antifouling paints for boats,[120] nonstick coatings for antennas and windows (e.g., to remove snow),[121] self-cleaning windshields for automobiles, metal refining, stain resistant textiles, nonsoil coatings for buildings,[122] the separation of water and oil, and in the textile industry. Recently, the antifouling properties of silica nanoparticles embedded in superhydrophobic polysiloxane materials were evaluated.[123]

Applications of BSMI materials also include: i) Transparent and antireflective coatings (these coatings can be applied to buildings or automobile windows, eyeglasses, optical windows for electronic devices, etc., ii) reduction in fluid drag (mainly due to the water-repellency of the surface which reduces interactions at the solid-water interface and generates a thin layer of air thereby establishing a new air-water boundary), iii) coatings that increase water supporting forces (provides extra supporting force for floating objects on water), iv) controlled transportation of fluids, v) prevention of water corrosion, vi) battery and fuel cell applications (bio-inspired materials provide solutions to problems in life-time expectancy and efficiency), vii) water-proof coatings for moisture sensitive electronic devices, viii) microcondensation (as observed for e.g., the superhydrophobic patterns on the back of the Namib desert bettle, *Stenocara Bettle*).

5. Summary and Outlook

In this review, a strategy for the design of bio-inspired, smart, multiscale, interfacial (BSMI) materials was proposed and examples of BSMI materials, in particular smart surfaces with two opposite wettability properties, were presented. Since the two complementary properties hydrophilicity and hydrophobicity were successfully utilized for the design of BSMI materials, other mutually compensating properties, i.e., conducting/insulating, convex/concave, p-type/n-type semiconductor, oxidizing/reducing, and ferromagnetic/anti-ferromagnetic could be used as factors for the design of BSMI materials in the future. Although some BSMI materials show potential for market-oriented industrial fabrication, the design of these materials is a complex problem involving many subtle changes on the surfaces and much more related work remains to be done on the theoretical analysis of new phenomena. The design, synthesis, and application of new kinds of organic or inorganic materials with stimuli-responsive properties are essential and important tasks to fulfill. Especially since complex real-life conditions require BSMI materials that can respond to dual- or multi-stimuli from the environment, e.g., temperature, solution pH, light, electrical fields, and so on.

Learning from nature is a constant principle for there are numerous mysterious properties in nature, which have developed over millions of years of evolution and will give us inspiration to develop novel functional interfacial materials.

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