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极端润湿性表面固体材料的制备与多功能化应用

王梦可，胡　怡，黄卫春*

南通大学化学化工学院，江苏　南通

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摘　要

液体接触角小于10°和大于150°的固体表面为极端润湿性固体表面。由于具有特殊的表/界面性能，这类固体表面在多个工业领域都表现出极高的应用前景，因此，研究和优化极端润湿性表/界面材料的制备方法，在实际生活中具有重要的意义。本文综述了几种典型的极端润湿性固体表面，包括超疏水表面、超双疏表面、超疏油/超亲水表面、超亲水/水下超疏油表面、超亲油/油下超疏水表面、超滑表面和润湿性可控的智能响应性表面，并探讨了极端润湿性表面在工业领域的多功能化应用，包括自清洁与防污涂层、透明与减反射涂层、油水分离与乳液分离、微流控、防结冰、防指纹、防雾、抗菌和防腐等方面。最后，本文从制备方法和实际应用的角度出发，对目前极端润湿性固体表面的发展做出了总结和展望。

关键词

润湿性，固体表面，多功能化，超疏水，超疏油

Preparation and Multifunctional Applications of Solid Surfaces with Extreme Surface Wettability

Mengke Wang, Yi Hu, Weichun Huang*

School of Chemistry and Chemical Engineering, Nantong University, Nantong Jiangsu

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Abstract

Due to their special surface/interface properties, the solids with extreme surface wettability, which

*通讯作者。

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possess a liquid contact angle below 10˚ or above 150˚, play vital roles in the fields of diverse industries. Therefore, the investigation and optimization of the fabrication of the solid surfaces with extreme surface wettability can largely promote the social development. In this paper, the typical solid surfaces with extreme surface wettability have been comprehensively summarized, including superhydrophobic surfaces, superamphiphobic surfaces, superoleophobic/superhydrophilic surfaces, superhydrophilic/underwater superoleophobic surfaces, superoleophilic/ underoil superhydrophobic surfaces, slippery surfaces, and intelligent responsive surfaces with tunable wettability. Moreover, the multifunctional applications of the solid surfaces with extreme surface wettability have been also investigated, including the self-cleaning and anti-fouling coatings, transparent and anti-reflective coatings, oil/water mixture separation and emulsion separation, microfluid devices, anti-icing, anti-fingerprint, anti-fogging, anti-bacteria, and anti-corrosion. At last, the developments and outlooks of the solid surfaces with extreme surface wettability were concluded from the points of the fabrication method and the practical applications.

Keywords

Wettability, Solid Surface, Multifunctional, Superhydrophobicity, Superoleophobicity

1. 引言

近几十年来，极端润湿性材料由于具有独特的表/界面性能，在诸多工业领域均表现出较高的应用价值，因此，极端润湿性固体表面的制备技术及其功能化应用成为目前表/界面功能材料研究方向的一个热门领域。本论文主要围绕几种极端润湿性表面，包括超疏水表面、超双疏表面、超疏油/超亲水表面、超亲水/水下超疏油表面、超亲油/油下超疏水表面、超滑表面和润湿性可控的智能响应性表面，做了系统的综述，并探索了上述几种极端润湿性材料的多功能化应用，包括自清洁与防污涂层、透明与减反射涂层、油水分离与乳液分离、微流控、防结冰、防指纹、防雾、抗菌和防腐等方面。最后，本文从制备方法和实际应用的角度出发，对目前极端润湿性固体表面的发展做出了总结和展望。

2. 极端润湿性表面的制备

2.1. 超疏水表面

超疏水表面是指水滴的表观接触角大于 150˚的固体表面。根据接触状态的不同，超疏水表面又可分为粘附性超疏水表面(Wenzel 态)和滚动性超疏水表面(Cassie-Baxter 态) [1] [2]。对应于上述两种状态，自然界中存在两个典型的例子：玫瑰花瓣和荷叶，如图 1 所示。水滴在玫瑰花瓣表面的接触呈 Wenzel 态，由于液体完全渗入到固体表面的粗糙结构中，即使玫瑰花瓣倒置，水滴依然不会从表面滚落；相反地，由于荷叶表面结构中空气的存在，通过轻微地倾斜荷叶表面，便可使水滴从荷叶表面滚落，对应于低粘附性的 Cassie-Baxter 态(滚动角小于 10˚)。

超疏水表面的制备方法一般包括微－纳结构的构筑和低表面能物质的改性两步，按途径可分为自上而下法(Top-down)和自下而上法(Bottom-up) [1]，自上而下法包括光刻法、化学刻蚀和阳极氧化法等[3] [4]，自下而上法包括水热法、静电纺织、电沉积、自组装法、模板法和溶胶－凝胶法等[5] [6]。两类制备方法各有优缺点，自上而下法可实现固体表面结构的精确可控，但适用面较窄，设备昂贵；自下而上

法操作灵活，适用面较广，但结构的生成较为随机，不可精确控制。图 2 为采用不同的方法制备得到的超疏水表面的 SEM 图片。

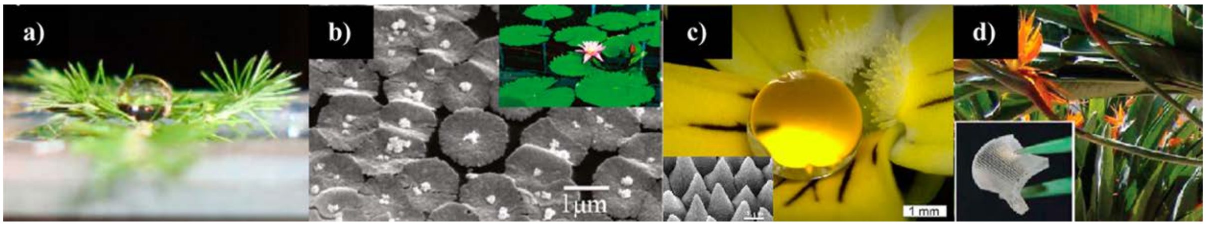

Figure 1. Examples of superhydrophobic plants [1]
图 1. 自然界中常见具有超疏水结构的植物表面

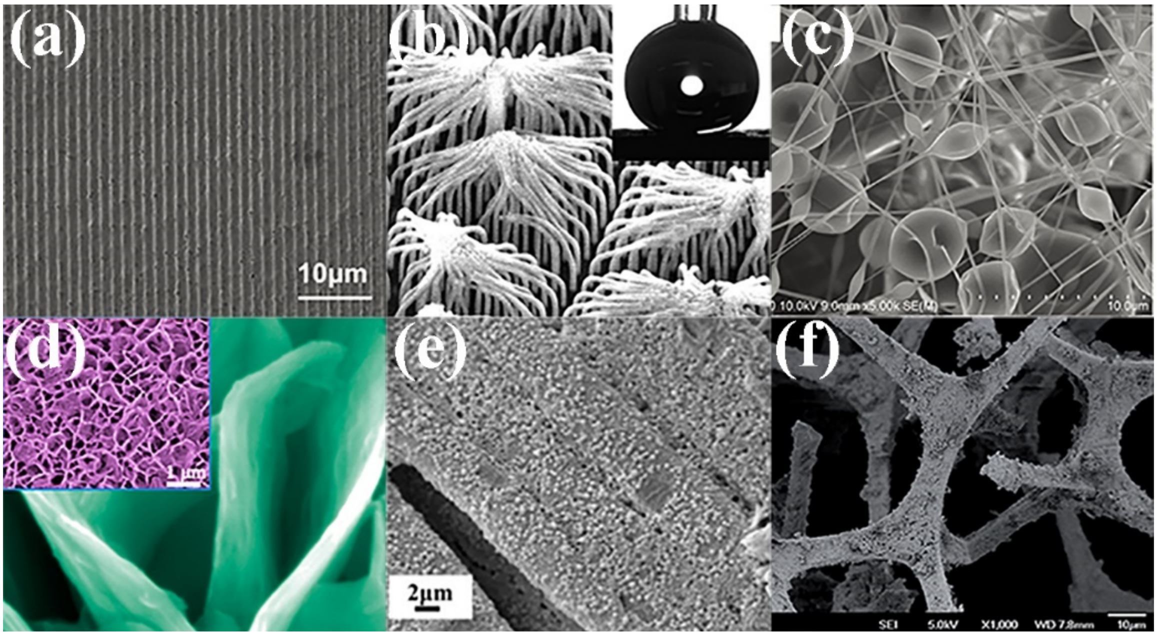

Figure 2. SEM images of superhydrophobic surfaces fabricated by (a) Laser lithography [7], (b) Reactive ion etching and metal-assisted chemical etching [8], (c) Electrospinning [9], (d) Electrodeposition [10], (e) Layer-by-layer assembly [11] and (f) Sol-gel method [12]
图 2. 不同方法制备得到的超疏水表面的 SEM 图片：(a) 光刻法[7]，(b) 活性离子和化学刻蚀两步法[8]，(c) 静电纺织[9]，(d) 电沉积[10]，(e) 自组装[11]和(f) 溶胶–凝胶法[12]

2.2. 超双疏表面

超双疏表面是指水和低表面能油类的表观接触角均大于 150˚的固体表面。由于油类液滴的表面张力低于水，一般来说，超双疏表面的制备需要更为复杂的微–纳结构和更低的固体表面能(通常需要长链氟化物的修饰) [13] [14]。因此，相比于超疏水材料，超双疏材料的制备从技术上和原理上都更难实现。2007年，Anish Tuteja 等人系统地梳理了超双疏材料的设计思路，并提出了满足超双疏性所需要的可插入式结构(re-entrantstructure)，如图 3 所示[15]。

2014 年，Liu 等人设计了一种特殊的双重可插入式结构(doubly reentrant structure)，如图 4 所示，这种结构不需要低表面能物质修饰，仅靠结构便能使原本亲水性的物质达到超双疏性[16]。经实验证明，具备这种双重可插入式结构的二氧化硅材料，对表面张力极低的全氟己烷同样具有优异的超疏液性能，并在 1000℃高温下仍能保持其超双疏性能。

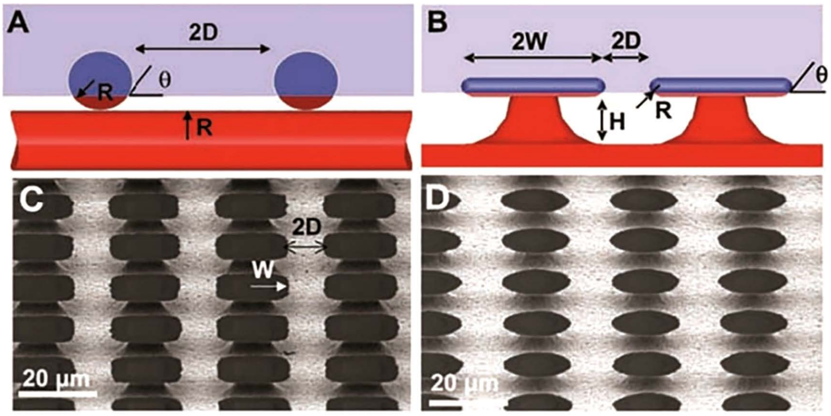

Figure 3. Cartoons of re-entrant structure: (a) Fibers and (b) Micro-hoodoos. SEM micrographs for two micro-hoodoo surfaces having (c) Square and (d) Circular flat caps [15]
图 3. 可插入式结构示意图：(a) 纤维状和(b) 微岩柱状。两种可插入式结构的 SEM 图片：(c) 方形帽和(d) 圆形帽[15]

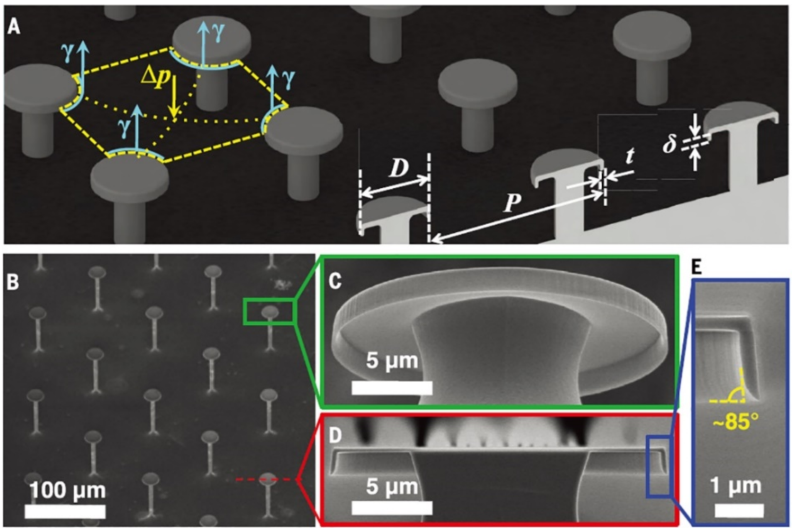

Figure 4. Design and fabricated results of SiO_2 surface [16]
图 4. SiO_2 表面的设计和制备[16]

2.3. 超疏油/超亲水表面

上一节超双疏表面中已经提到，由于油类的表面能较水低，因此能够疏油的表面一般也具有疏水性。然而，也存在一类固体表面，能同时具备超疏油和超亲水两种极端润湿性。2012 年，我们团队首次制备出了超亲水/超疏油表面，图 5 为相应的化学反应式和润湿性图片[17]。作者采用二烯丙基二甲基氯化铵和全氟辛酸钠进行反应，在固体表面同时引入了亲水性基团和低表面能的氟化碳链，制备出了超疏油/超亲水的固体表面。需要指出的是，极性水分子与亲水性基团的接触需要一定的时间，因此这类固体表面的超亲水性往往在与水接触一定时间后才得以显现(图 5(b))。

2018 年，潘昀路教授团队从理论上系统分析了超疏油/超亲水表面的本质，并设计实验制备出了超亲水/超疏油表面，将其应用于油水分离领域[18]。图 6 为作者提出的超亲水/超疏油表面与超双疏表面的不同之处示意图。从图中可以看出，与超双疏表面不同，当水接触到超亲水/超疏油表面时，由于水分子体积较小，可穿过氟化碳链与下层亲水性基团接触，固体表面呈现超亲水性；与此同时，低表面能的非极性油类则由于氟化碳链的阻碍不能进入材料内部，固体表面宏观上表现出超疏油性。

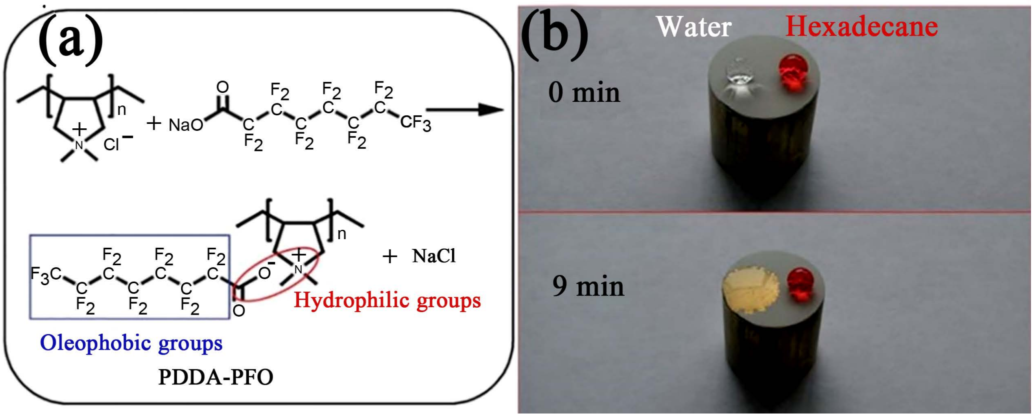

Figure 5. (a) Chemical reaction and wettability of the first reported superoleophobic and superhydrophilicsurface [17]
图 5. 首例报导超疏油/超亲水表面的(a) 反应式和(b) 润湿性图片[17]

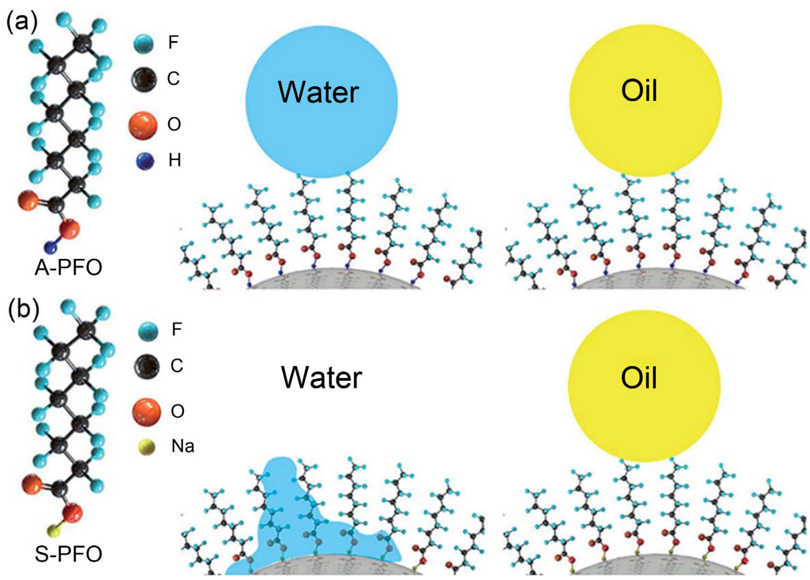

Figure 6. (a) Superamphiphobic surface prepared by perfluorooctanoic acid and (b) superoleophobic/superhydrophilic surface prepared by sodium perfluorooctanoate [18]
图 6. (a)全氟辛酸制备得到的超双疏表面和(b)全氟辛酸钠制备得到的超疏油/超亲水表面[18]

2.4. 超亲水/水下超疏油和超亲油/油下超疏水表面

超亲水/水下超疏油性和超亲油/油下超疏水性往往同时出现，具有这两种性质的固体表面往往含有大量的亲水基团或极性基团，并伴有粗糙的微纳结构[19]。当这类固体表面先接触到水时，由于超亲水性，水分子会完全浸润固体表面，并且在固体表面的微纳结构中存留一定体积的水，形成水阻隔层，进而达到水下超疏油性；另一方面，当这类固体表面先接触到油类时，由于超亲油性，油类完全浸润固体表面，并且在固体表面的微纳结构中存留一定体积的油类，形成油阻隔层，进而达到油下超疏水性[20]。图 7 为超亲水/水下超疏油表面的示意图，固体表面微纳结构的存在为液体的存储提供了结构支持[21]。

2.5. 超滑表面

在极端润湿性领域内，固体表面的超滑行为是指将固体表面倾斜较小的角度(小于 10°)，液滴从固体表面滑落的现象。与 Cassie-Baxter 态超疏水性不同的是，超滑固体表面液滴的去除是以滑动方式进行的，

而非滚动方式。目前超滑表面的实现方式主要有两种，一种是 Joanna Aizenberg 等人提出的油注入型超滑固体表面(SLIPSs, slippery liquidinfusedporoussurfaces)，另一种是 Atsushi Hozumi 等人提出的共价接枝烷基链型的类液超滑固体表面，两种超滑表面疏液原理示意图如图 8 所示。

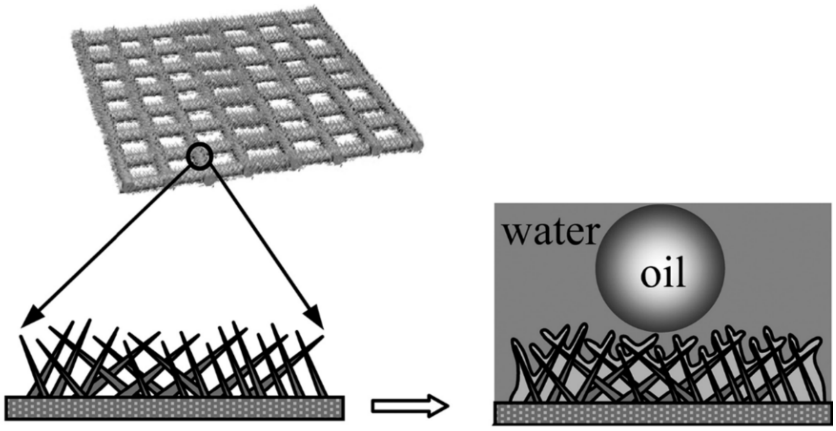

Figure 7. Schematic illustration of oil wetting on membrane with a micro/nano-hierarchical structure in water [21]
图 7. 水下环境中，油滴在微纳多级结构固体表面的润湿行为示意图[21]

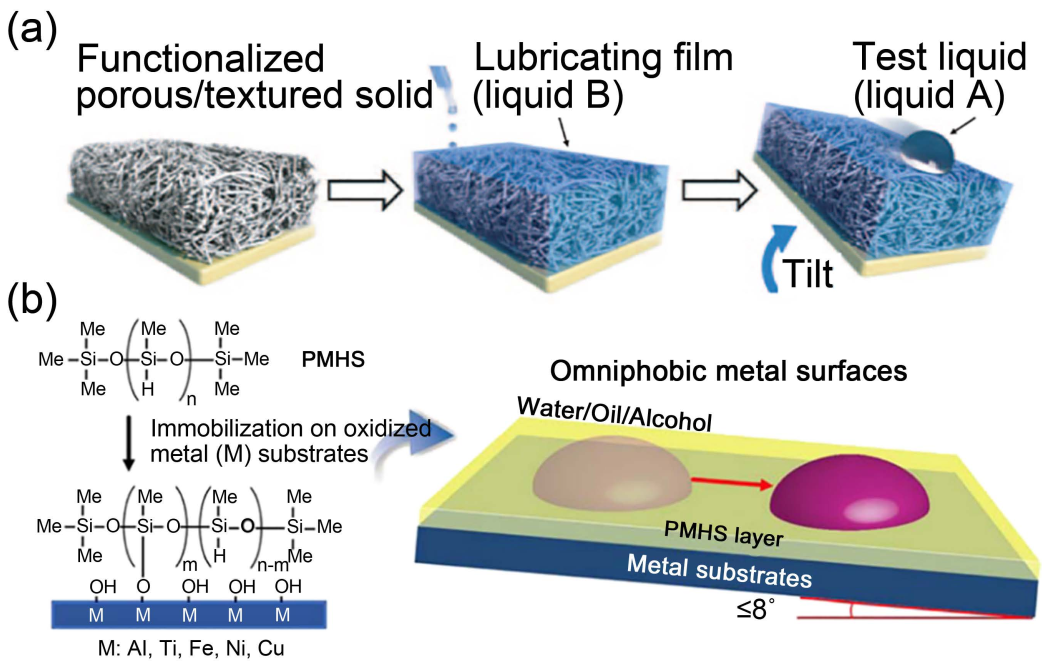

Figure 8. (a) SLIPSs [22] and (b) Covalently attached liquid-like surfaces [23]
图 8. (a) 油注入型[22]和(b) 烷基链接枝型超滑固体表面[23]

2011 年，Joanna Aizenberg 等人通过将全氟聚醚或硅油类低表面能液体注入表面具有微纳粗糙结构的基底中，制备得到了油注入型超滑表面[22]。这类表面的典型特征有二：其一是基底需要具有较好的多孔结构，用以容纳和吸附注入的油类物质；其二是注入的油类需具备难挥发性和较低的表面能[24] [25]。图 8(a)为油注入型超滑固体表面的制备和液滴滑动方式示意图。

另一类超滑表面是表面接枝烷基链的类液固体表面，示意图如图 8(b)所示。Atsushi Hozumi 及其团队在这类表面的制备方面做了大量的工作[23] [26] [27]。这类表面的典型特征是，作为基底的固体表面较

为平滑，粗糙度极低，另一方面，含烷基链的分子与基底表面活性基团共价接枝，形成类液层，厚度多为 10 nm 以内。2016 年，McCarthy 团队提出了一种快速制备此类表面的方法，制备时长控制在几分钟内，所得超滑表面的接触角滞后非常低，倾斜表面 2˚左右便可使液滴从固体表面滑落[28]。

2.6. 润湿性可控的智能响应性表面

近年来，随着智能化概念的提出和发展，有关润湿性可控的固体表面方面的研究开始受到越来越多的关注。所谓润湿性可控的响应性表面，是指固体表面的润湿性在受到外界环境刺激下发生转变，并且转变过程具有可逆性。目前有关润湿性可控表面的研究报道中，涉及到的外界刺激源主要包括 pH 值[29]、温度[30]、电场[31]、UV 光[32]、CO_2 气体[33]和 NH_3 气体[34]等。图 9 为上述外界刺激下，固体表面润湿性可逆转变的原理示意图。

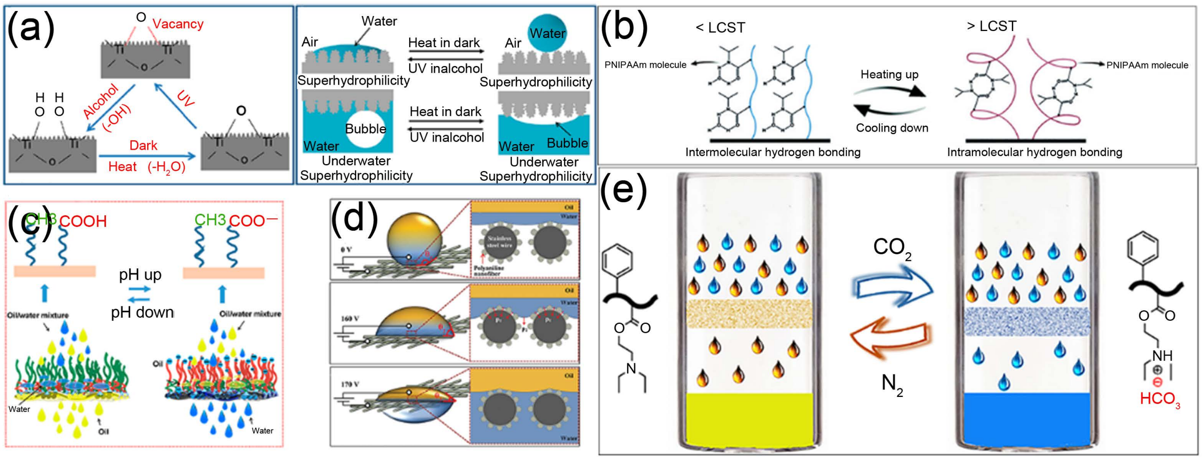

Figure 9. Switchable wettability under different stimulations: (a) UV-light [32], (b) Temperature [30], (c) pH [29], (d) Electric field [31] and (e) CO_2 [33]

图 9. 刺激响应下的润湿性转变：(a) UV 光[32]，(b) 温度[30]，(c) pH 值[29]，(d) 电场[31]和(e) CO_2 气体[33]

3. 具有极端润湿性表/界面材料的功能化应用

3.1. 自清洁与防污

Cassie-Baxter 型超疏水表面与水接触时，具有特殊的固－液－气三相复合式接触的界面性能，水滴和 Cassie-Baxter 型超疏水表面之间的粘附力较低，极易从固体表面滚落。当该类型材料表面沾有灰尘、泥土等污染物时，水流经过超疏水表面时会带走材料表面粘附的污染物，因此，具有 Cassie-Baxter 型超疏水表面的固体材料往往兼具自清洁和防污功能[35]。图 10 为超疏水涂层的自清洁和防污过程示意图[36]。

3.2. 透明超疏涂层与减反射涂层

将固体材料外表面施加一层透明涂层，可在不改变基底特性的基础上调控其表/界面性能，因此，研究和优化透明涂层的制备对固体材料在特殊领域的应用起到重要的作用。透明超疏水涂层和透明超双疏涂层由于具有自清洁、防污等特性，在光伏产业、玻璃工业等领域逐渐受到重视。然而，由于超疏水和超双疏表面粗糙微纳结构的存在，超疏水/超双疏涂层的制备过程中往往会造成材料透明度的下降。另一方面，由于在材料表面构筑了多级微纳结构，超疏水和超双疏涂层的机械稳定性和耐久性会存在一定程度的降低。因此，如何同步提高超疏水涂层和超双疏涂层的透明度与稳定性，目前仍需要进一步的研究。图 11 为部分研究工作中制备得到的透明超疏涂层[37] [38] [39]。

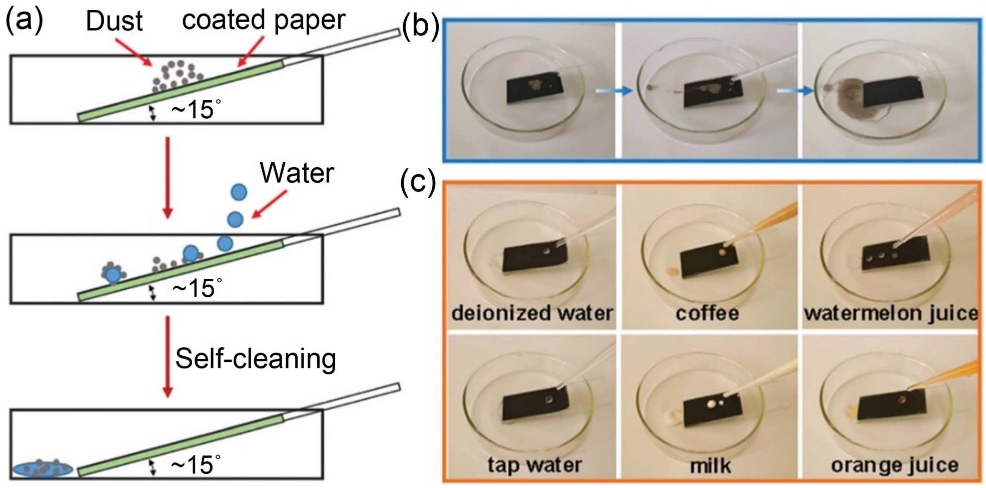

Figure 10. (a) Schematic illustration; (b) Optical photographs of self-cleaning test on superhydrophobic surface; (c) Anti-fouling processes on superhydrophobic surfaces [36]

图 10. (a)示意图；(b)超疏水表面自清洁过程的光学图片；(c)超疏水表面的防污过程[36]

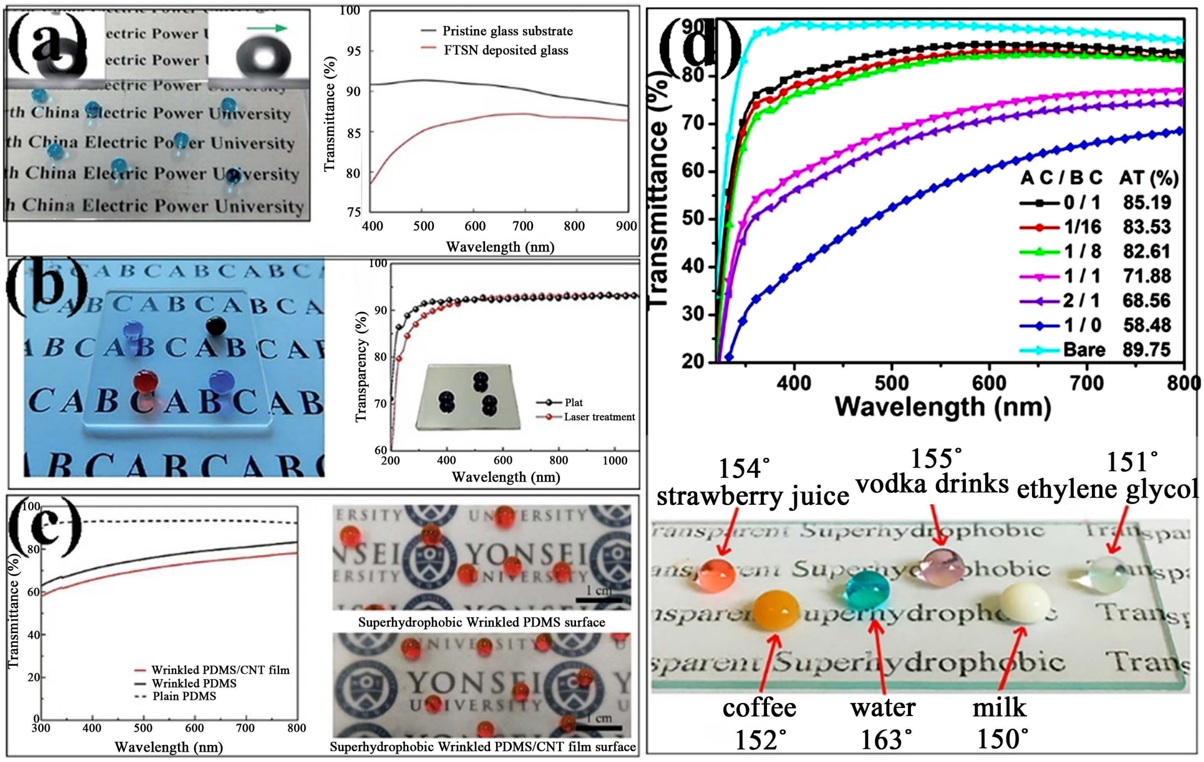

Figure 11. (a)~(d) Partly reported transparent superlyophobic coatings [37] [38] [39]

图 11. (a)~(d)部分文献中报道的透明超疏涂层[37] [38] [39]

由于建筑外窗用玻璃反射现象较为严重，现代城市中光污染普遍存在，给人们生活上造成了困扰，因此，具有减反射功能的超疏涂层在玻璃工业存在非常大的应用价值，可有效减少光污染，同时降低清洁成本。减反射材料的原理，是通过特殊的结构设计，将材料表面涂层的折射率从定值变为层层递进的变值，理想的减反射涂层，其折射率需要在空气和基底的折射率之间实现逐渐变化。由于涉及到的结构设计过于精细，减反射超疏涂层的制备目前还存在一定的难度。图 12 为部分目前报道的减反射涂层[40] [41] [42] [43]。

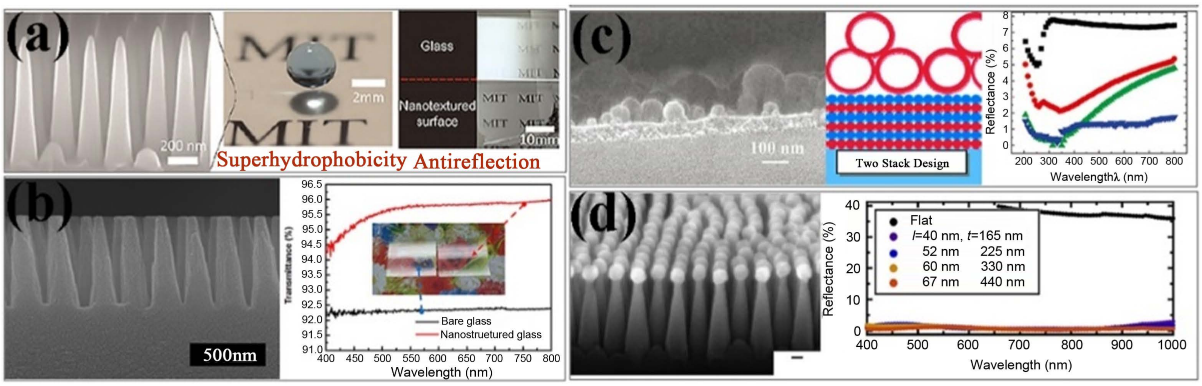

Figure 12. (a)~(d) Partly reported antireflective coatings [40] [41] [42] [43]
图 12. (a)~(d)部分文献中报道的减反射涂层[40] [41] [42] [43]

3.3. 油水分离与乳液分离

极端润湿性材料对水和油类分别具有不同的亲和性，因此相比于传统分离材料，极端润湿性材料在高效、快捷的油水分离和乳液分离领域占有举足轻重的地位。目前关于极端润湿性材料在油水分离领域的应用研究较为热门，主要围绕超亲水/水下超疏油材料、超亲油/水下超疏水材料和超疏水/超亲油材料这几种类型。上述几种不同类型的极端润湿性材料，对水和油类的亲和程度各异，因此具有各自的油水分离机制，图 13 为几种类型的极端润湿性材料不同的油水分离与乳液分离机制[44] [45] [46] [47] [48]。

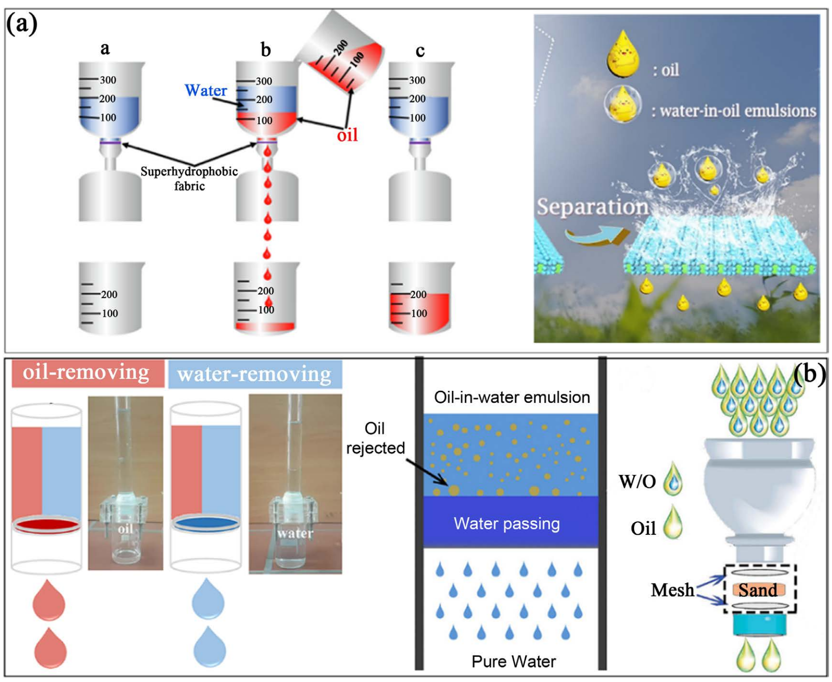

Figure 13. Schematic diagram of oil/water mixtures and emulsions separation processes with (a) Superhydrophobic/superoleophilic materials [44] [45], (b) Superhydrophilic/underwater superoleophobic and superoleophilic/under oil superhydrophobic materials [46] [47] [48]
图 13. 油水分离和乳液分离机制：(a) 超疏水/超亲油材料[44] [45]，(b) 超亲水/水下超疏油和超亲油/油下超疏水材料[46] [47] [48]

超亲水/水下超疏油材料往往兼具超亲油/油下超疏水性，这类材料适用范围较广，可用于水/重油混

合物、水/轻油混合物、油包水乳液和水包油乳液的分离。相对来说，超疏水/超亲油材料多用于分离水/重油混合物和油包水乳液，而且由于其超亲油性，该类材料在分离过程中容易被油类堵塞，加大了循环利用的难度。综上所述，超亲水/水下超疏油和超亲油/油下超疏水材料在油水分离和乳液分离方面的性能更为优异，可选择范围更为广泛。

3.4. 液滴的定向流动与无损转移

通过表面处理，可赋予固体表面润湿程度各向异性，进而实现该类固体表面在微流体器件方向上的应用，如固体表面的图案化、液体的定向传输和无损转移等。图 14 为利用极端润湿性表面制备的多功能微流体器件。Liu 等[49]利用一种无需掩膜的微等离子体枪技术，在超疏水铝片上构筑了高粘附亲水性的图案，在超疏水表面上实现了水流体的图案化(图 14(a))。Tuteja 团队[50]在纸张上正反两面分别构筑了多个微流体通道，经过特殊处理后，各个流体通道对不同表面张力的液体具有不同的亲和性，在同一固体表面实现了不同表面张力液体的同步输送(图 14(b))。Jang 等[51]在不同聚合物表面构筑了特殊的多级结构，利用聚合物基底的本征润湿性，实现了液滴的定向传输(图 14(c))。

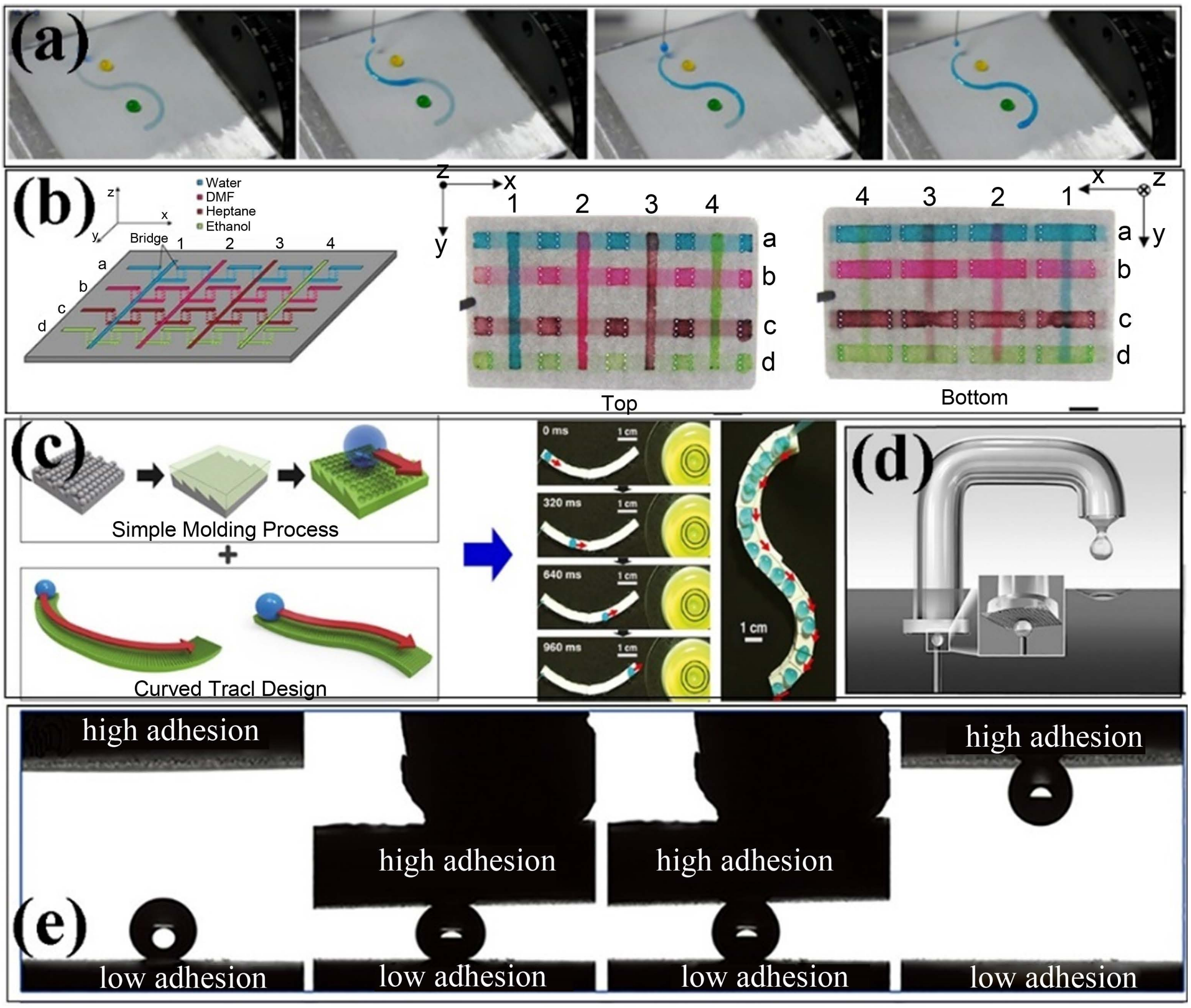

Figure 14. Patterning [49], microfluidic channels [50], directional droplet movement [51] [52] and no-loss droplet transfer [53] on the surface of superwetting solids

图 14. 极端润湿性固体表面的图案化[49]，微流体通道[50]，液滴定向运输[51] [52]和无损转移[53]

江雷院士及其团队[52]设计了一种可用于水下油类收集的器件，以油滴自由能的自释放作为驱动力，利用超疏油网实现了水下油滴的自发收集，如图 14(d)所示。吉林大学刘燕教授[53]利用不同固体表面与水滴之间粘附性的差异，实现了水滴从低粘附性超疏水固体表面(Cassie-Baxter 型超疏水)到高粘附性超疏水固体表面(Wenzel 型超疏水)之间的无损转移，转移过程如图 14(e)所示。

3.5. 防结冰涂层

应用于防结冰领域的极端润湿性固体表面主要有两种：超疏水涂层和油注入型超滑涂层，两种类型的极端润湿性涂层存在不同的防结冰机制。超疏水涂层在水滴结冰前，由于表面的超疏水性会引起水滴的滚落，因此能有效防止固体表面水的聚集，抑制水结冰成核。另外，超疏水表面水滴结冰后，由于与涂层之间的粘附力较低，通过外力可轻易将冰去除，但会对涂层造成一定的破坏，致使其性能下降。超滑涂层的除冰机制与超疏水涂层不同，主要作用在冰形成之后，涂层表面微结构中注入的低表面能润滑油，可在冰形成之后依然保持液态，从而使其表面的冰可轻易地去除[54]。

中科院化学所的王健君研究员近年来深入研究了冰晶成核的机理，为防结冰材料的发展做出了重要的贡献[55] [56] [57]。2014 年，其团队总结了目前防结冰涂层的研究现状，为防结冰材料的设计和领域的发展提供了重要的理论依据，图 15 为其总结的几种防结冰机制[54]。

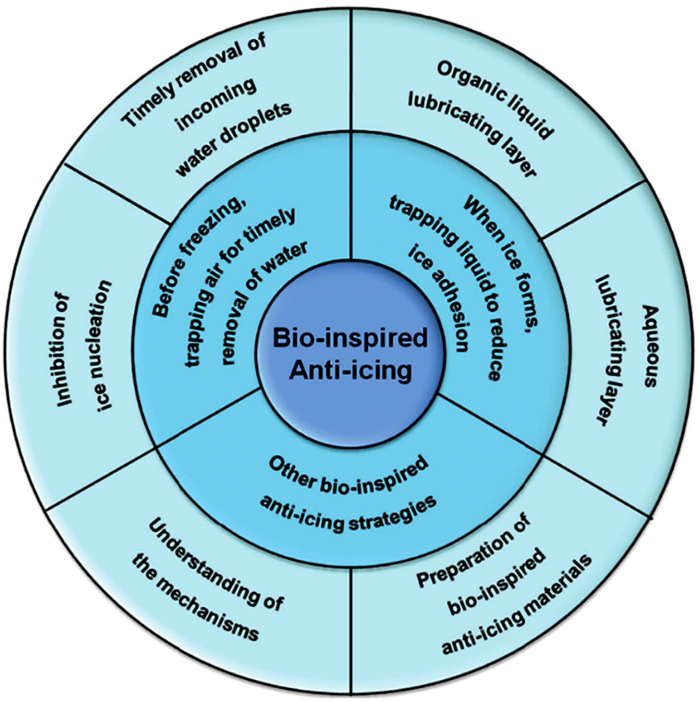

Figure 15. Three main categories of recently developed bioinspired anti-icing strategies [54]
图 15. 近期报导的受生物启发的三类主要的防结冰策略[54]

3.6. 防指纹与防雾

超滑表面存在一层流动性或类液性的低表面能润滑油，因此具有一定的防指纹功能，可用在手机屏幕、电脑显示器等光学器件上[58]。防雾功能主要伴随超亲水涂层出现，在起雾环境中，超亲水涂层能在固体表面凝聚成一层“水膜”，减少光的散射，从而达到防雾的效果[59] [60]。图 16(a)和图 16(b)分别为防雾和防指纹涂层效果的光学图片[61]。

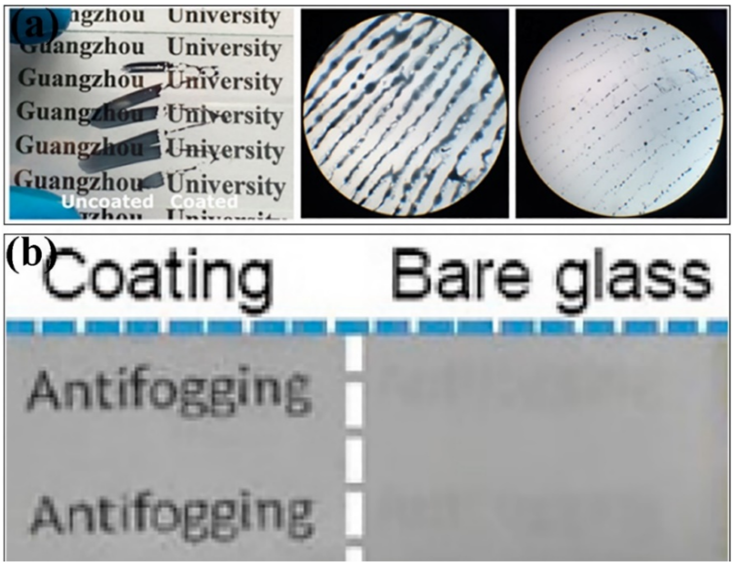

Figure 16. Anti-fingerprint coating [58] and anti-fogging coating [61]
图 16. 防指纹涂层[58]和防雾涂层[61]

3.7. 抗菌与防腐

Cassie-Baxter 型超疏水表面与水滴之间具有极低的粘附力，因此也能有效抑制水溶液中细菌的依附，进而抑制固体材料表面细菌的繁殖与生长[62] [63]。另外，由于水分子难以进入到超疏水材料内部，具有超疏水表面的材料在含有腐蚀性离子的水溶液中，其耐腐蚀性显著提高，使用寿命得以延长[64] [65]。

4. 总结与展望

近几十年来，有关极端润湿性表面的研究热度逐年增高，另外，具备极端润湿性表面的固体材料在各工业领域的功能化应用研究也逐渐开始受到关注。例如，超疏水涂层在自清洁、防结冰、抗菌、防腐蚀和油水分离方面的应用；超双疏涂层在防油污和抗油冲击方面的应用；超滑涂层在防指纹、防腐蚀和防油污方面的应用；超亲水涂层的防雾功能化应用；超浸润材料在油水分离和乳液分离领域的应用等。

目前关于极端润湿表面的功能化研究取得了一定的进展，但该领域仍然存在一些问题亟待解决：其一，除透明超疏水涂层外，彩色超疏水涂层的制备对绘画、涂料、建筑等相关领域的发展同样起到促进作用，但目前关于颜色可控的彩色超疏水涂层的研究较为缺乏；其二，相比于具有单一功能的极端润湿性材料，材料的多功能化能显著拓宽其应用领域，满足不同工业领域的应用需求，目前的研究进展中，关于极端润湿性材料的多功能化应用还需进一步探索；其三，超润湿材料在油水分离领域具有巨大的应用价值，可替代传统分离材料，实现油水分离的高效化、便捷化，然而目前能同时满足不同场景下的多通道油水分离材料报道相对较少，另外，乳液分离的困难性仍需进一步克服。

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