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飞秒激光制备耐久型超疏水表面及其应用的研究进展(特邀)

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摘　要:仿生超疏水表面在油水分离、防结冰、自清洁等方面具有广阔的应用前景。但是由于其表面结构的脆弱所造成的不稳定性,使其在应用时受到较大限制。飞秒激光作为一种通用的微纳加工方法,在超疏水表面的制备中有许多明显的优势,并且适用于几乎任何硬质材料的加工。本文从浸润性的基本模型出发,分析了耐久型超疏水表面的特点,针对耐久型超疏水表面的飞秒激光制备方法以及应用进行了概述,从聚合物、玻璃以及金属等物质的超疏水表面的飞秒激光制备进行了归纳。对超疏水表面在油水分离、防结冰、自清洁等方面的应用研究进行了综述。最后总结了利用飞秒激光制备耐久型超疏水表面所面临的挑战。

关键词:耐久性;超疏水表面;飞秒激光;油水分离;抗冰
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0 引言

经过了自然界的不断进化和演变,许多生物进化出赖以生存的超疏水表面,比如具有自清洁性能的荷叶表面、能够在水面爬行的水黾等[1-5]。直到20世纪末,人们才对超疏水表面进行了深入研究,发现形成超疏水表面的关键在于材料表面的化学成分和微观结构[6-11]。通过调控材料表面的化学成分和微观结构,人们在不同材料上研究并制备出超疏水表面,给能源、环境、健康带来了巨大的影响。受这些自然界超疏水表面的启发,通过各种方法调控材料表面化学成分和微观结构,比如机械方法、光刻法、化学刻蚀、模板法、气相沉积、电化学刻蚀、电纺丝法、自组装法以及喷涂法等等[12-21],已经制备出了多种超疏水表面。目前,超疏水表面已经被广泛应用于抗液、自清洁、液滴操控、油水分离、抗冰等领域[22-31]。然而超疏水表面的微观结构在外力作用下容易发生应力集中而被破坏,表面的化学成分也会在外界物质的侵蚀下降解,导致表面的超疏水性能减弱或者消失,这也成为限制超疏水表面在各种领域应用的主要障碍[32]。超疏水表面的耐久性一方面与表面结构和化学成分有关,另一方面也受限于基体材料本身的耐久性。许多传统制备微纳结构的方法能够用来实现材料的超疏水性,但这些方法不同程度地都会受到其方法本身的局限,比如复杂的制备流程、材料的局限性,缺乏灵活性等。发展出一种通用、简便、能够用于多种材料的方法制备耐久型极端浸润性结构表面仍然是一个巨大的挑战。

飞秒激光作为一种超快脉冲激光,具有超短脉冲以及超高的峰值功率[33]。近年来,飞秒激光在现代超

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精密制造领域中扮演着越来越重要的角色。飞秒激光加工具有高空间分辨率、低热效应以及非接触加工等特点[34]。同时，飞秒激光加工几乎能够应用于所有材料，并且能够精确的在其表面设计并构建微纳结构。由于表面微纳结构对固体材料的浸润性有着决定性影响，通过在材料表面制备各种微纳结构，飞秒激光加工能够满足不同的浸润性需求[35-37]。在调控材料浸润性方面，飞秒激光加工有着强大的优势与能力。

本文从浸润性基础理论出发，分析了限制超疏水表面应用的耐久性问题，对飞秒激光制备耐久型超疏水表面的研究进展进行了综述，包括在多种材料超疏水表面的制备，以及超疏水表面在各个领域的应用。最后对飞秒激光制备耐久型超疏水表面进行了展望，以期为飞秒激光制备耐久型超疏水材料的发展提供参考。

1 背景

1.1 浸润性基本理论

当液滴与固体表面接触时，固液气三相会在表面张力的作用下达到平衡，形成三相接触线。其中，固液接触面、气液接触面经过三相点做切线所形成的夹角，称为接触角（Contact Angle，CA）[38-39]。对于极端浸润性而言，当接触角小于10°时，表面称为超亲水表面；当接触角大于150°时，表面称为超疏水表面。接触角反映的是固体表面的静态浸润状态，而动态浸润状态通常用滑动角（Sliding Angle, SA）来表征[40]。在样品逐渐倾斜，水滴能够靠自身重力脱离固体表面时表面与水平面的夹角称为滑动角。通常，大的滑动角能够反映出表面具有高粘滞性，小的滑动角能够反映出表面的低粘滞性。

Young氏方程描述了理想状态下光滑表面的界面能对浸润性的影响，如图1(a)所示。液滴的接触角为[41]

$$\cos\theta=\frac{\gamma_{SA}-\gamma_{SL}}{\gamma_{LA}}$$

式中，γ_{SA}、γ_{SL}、γ_{LA}分别是固气、固液和液气的表面自由能。但绝大多数时候，固体表面都不是绝对光滑的，即表面存在不同程度的粗糙度，这对材料表面的润湿性有重要影响。考虑到粗糙度对表面浸润性的影响，在固体表面被润湿时，表面粗糙结构能够显著增加固液接触面积，如图1(b)所示[42]，改进Young氏方程，引入粗糙度的概念(R)[43]

$$\cos\theta^{*}=\frac{R\left(\gamma_{SA}-\gamma_{SL}\right)}{\gamma_{LA}}=R\cos\theta$$

式中，θ^{*}和θ分别为液滴在粗糙表面和对应的理想光滑表面的接触角。R为粗糙度因子，为真实表面积与其投影面积的比值。此模型中，固液接触时液体会在固体表面的粗糙结构中完全填充。从上式可以看出：固体表面的粗糙微结构能够放大其对应的本征浸润属性。即使得本征亲水表面更加亲水，使本征疏水材料表面更加疏水。

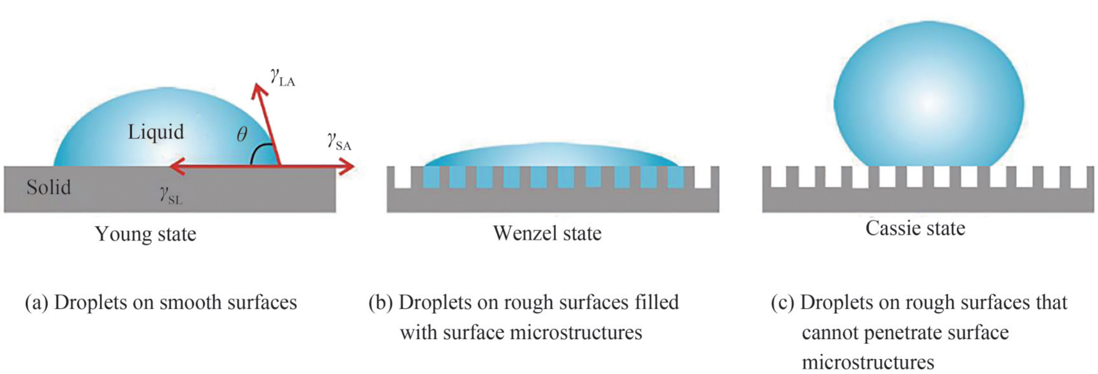


图1 液滴在固体表面的典型湿润状态
Fig. 1 Typical wetting state of droplets on solid surface

此外，还存在另一种浸润模型，Cassie模型[44]。Cassie模型中，如图1(c)所示，表面粗糙微结构中液体与固体的接触面之间存在一空气层，其接触角满足

$$\cos\theta^{*} = f\cos\theta + f - 1$$

式中，θ为Young氏接触角，f为液滴所接触的表面部分占整体表面的面积分数。

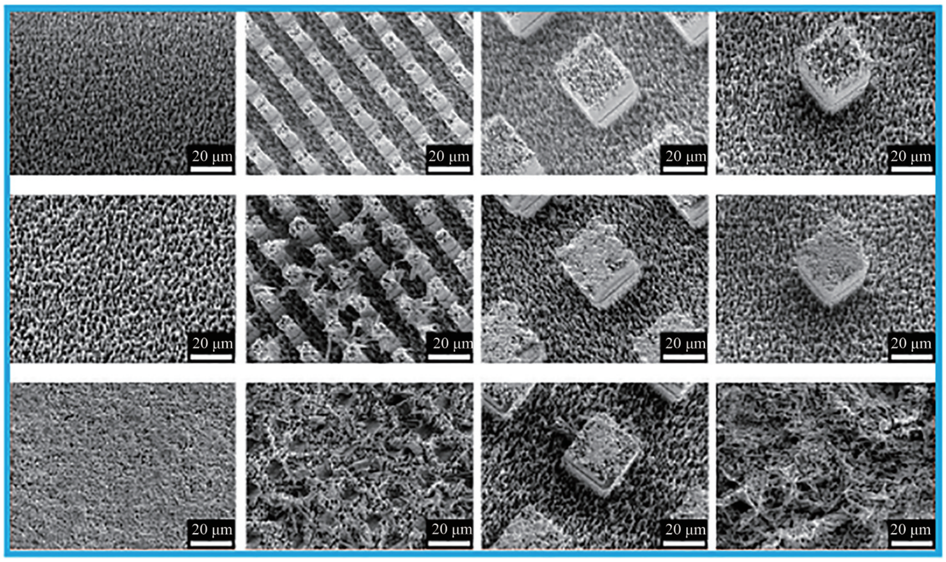
在实际中，表面对液滴的粘滞性表面取决于两者的实际接触面积，处于Wenzel状态的表面一般对液滴展现出高的粘滞性；对于Cassie状态，由于中间空气层的存在，使得固液接触面积非常小，从而表现出很低的粘滞性。

1.2 耐久型超疏水表面的特点及表征方法

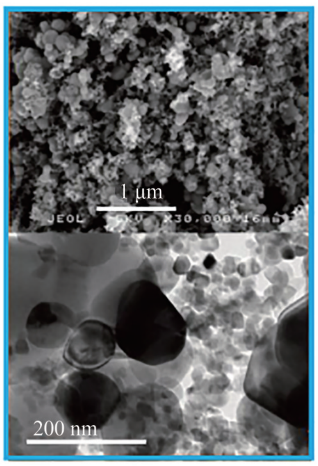
超疏水表面能够应用在实际生活中的关键是提高其机械稳定性和化学稳定性从而延长其服役时间，因此制备耐久型超疏水表面已成为近年来的重点研究方向。通过浸润性理论，我们知道适当的表面微结构层以及低表面能化学物质是构建和维持材料表面超疏水特性的两个决定性因素，缺少任何一个因素都会降低表面的超疏水性能[45]。而针对这两点，目前耐久型超疏水表面的表征方法可以对应归纳为两方面，机械耐久性表征和化学耐久性表征[46]。首先，对于机械耐久性的评价，主要是评价表面微纳米结构的机械磨损耐久性，造成表面微结构损失的方式主要有三种，分别是横向剪切力破坏、微纳组织与基体结合力的弱化、外界物质对表面组织的直接冲击等。对超疏水表面机械耐久性表征的具体测试方法包括摩擦磨损测试、胶带剥离、硬度和附着力测试、冲击试验以及落砂/落水测试等，通过这些测试方法能够定量的表征超疏水表面的机械耐久性[47-49]。其次，化学耐久性表征主要是评估超疏水表面是否能够维持低表面能状态。低表面能状态是由低表面能物质维持，而低表面物质在长时间的使用过程中又会以不同方式进行损耗。主要损耗形式有：伴随表面微观结构的磨损而损耗、低表面能物质与外界环境物质反应而失效以及低表面能物质随着长时间使用而老化失效。其中，伴随表面微观结构的磨损而损耗这一点与机械耐久性的评价方法相同。而其他两种损耗形式的化学耐久性的评价方法包括紫外辐照测试、温度测试、酸碱溶液浸泡测试、高温高湿环境测试、溶液浸泡和循环洗涤等[50-52]。一般来说，综合评价超疏水表面的耐久性，往往是将几种评价手段组合进行[53-54]。

目前，已经发展出了几种不同的策略来制备耐久型超疏水表面。许多研究已经证明，具有多级微纳米复合结构的超疏水表面，要比单一尺度微米级或者纳米级微结构具有更高的机械耐久性[55-56]。GROTEN J等研究了表面的微米结构与纳米结构结合以后表面耐磨性对润湿性能的影响[57]。将微米尺度的柱状结构与纳米微结构相结合，结果表明在一定的比例下，两种结构的结合能够使得材料表面在保持超疏水性的同时也拥有良好的耐磨损性（图2(a)）。近来，也有研究提到将表面微结构通过粘结层加固在材料表面也能够提高超疏水表面的耐久性。LU Y等将疏水的纳米颗粒制备成成胶黏剂，通过喷涂、浸涂或挤压等方式将胶黏剂与基体材料结合[58]。通过胶黏剂这种形式，既增加了微结构与基体的结合强度，还能在表面受到外力作用时起缓冲效果，从而对微纳米结构进行物理保护，对超疏水表面的机械耐久性明显提升（图2(b)）。此外，通过构建表面保护层对微纳米结构进行物理保护，由此提高其机械耐久性近来也被提出。WANG D等通过在两种不同长度尺度上分别构建表面结构实现了机械耐久性非常出色的超疏水表面，纳米结构提供超疏水性能，微观结构设计作为“铠甲”对纳米颗粒进行保护，从而保证了其在工作过程中的耐久性（图2(c)）[59]。最后，构建自修复型超疏水表面也成为提高耐久性的一种有力手段，不同于前面几种策略，自修复策略主要聚焦于对受损后的超疏水功能的恢复，从而延长其使用寿命。BAI X通过飞秒激光在形状记忆聚合物表面制备出分层微柱结构的超疏水表面，表面结构受外载荷作用后，超疏水性能降低，但是经过简单的加热过程即可恢复原有的超疏水性能，并且具有优异的抗磨损、胶带剥落、抗紫外线照射以及防酸碱腐蚀性溶液腐蚀的性能（图2(d)）[60]。

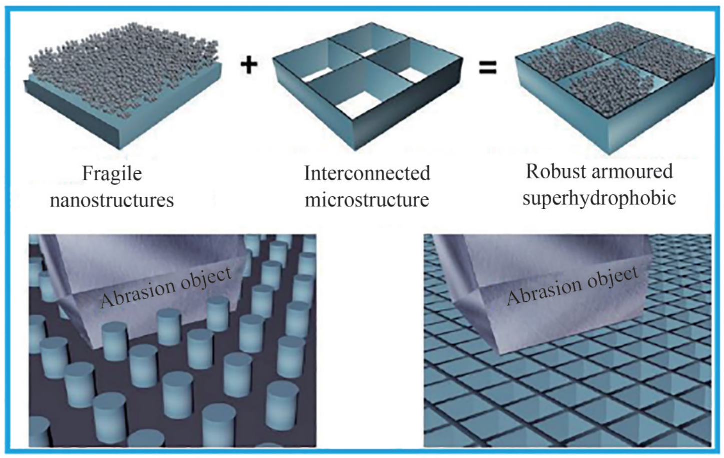
此外，基体材料的本征性能也会严重影响所制备的超疏水表面耐久性。然而，如果材料本身具备较高的机械耐久性和化学稳定性，又会造成构筑表面微结构层时的困难。面对不同应用需求，制备超疏水表面所需的材料不尽相同，包括半导体、聚合物、脆性材料和金属等。这些材料对应的超疏水表面所需的制备方法却不尽相同，飞秒激光微纳加工这一方法的出现大大简化了这一问题。



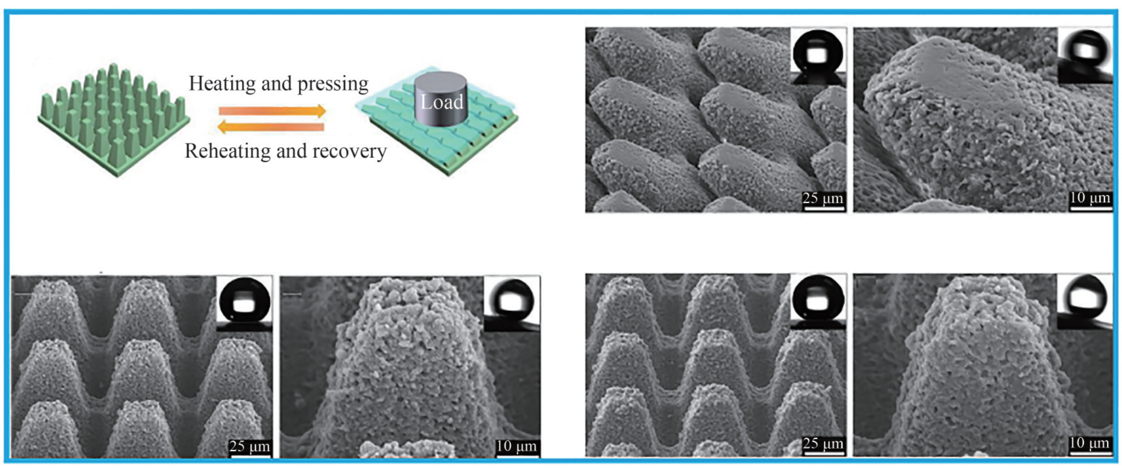
(a) Surface morphology combined with micron and nanostructure



(b) Nanoparticles and adhesives



(c) Nanostructures wrapped in protective microstructure 'armor', protective effects of different 'armor' structures



(d) Morphology and contact angle changes of SMP original micropillar array, compression deformation micropillar array and photoresponse recovery micropillar array fabricated by femtosecond laser

图2　制备耐久型超疏水表面的几类策略[57-60]

Fig. 2　Several strategies for processing durable superhydrophobic surfaces[57-60]

1.3 飞秒激光微纳加工

飞秒激光已经被证明为一种非常有效的用于超疏水表面制备的工具。这是由于其超短的脉冲宽度(10^{-15} s)以及超高的峰值能量(10^4 W)[61]。这种独特特性使得飞秒激光微加工与传统加工技术相比表现出许多明显的优势,例如在烧蚀区周围形成最小的热影响区,非接触式制造,高空间分辨率以及加工材料的广泛性[62]。飞秒激光与材料表面作用时,会形成材料的"冷"蚀刻,这一过程大大降低了热效应,而在以往的激光加工中,热效应通常会导致加工精度低和材料的选择性差等问题[63]。飞秒激光与固态基体材料的相互作用是一个复杂的非线性过程。只有在焦斑中心附近的有限区域,激光能量高于多光子反应阈值的区域才能够进行加工,从而实现材料的超精细微纳米加工。非线性过程也使得飞秒激光能够对各种透明以及非透明材料进行烧蚀,包括半导体、金属、聚合物、脆性材料、陶瓷和生物材料等[64]。飞秒激光能够直接在这些材料表面诱导出微纳米结构,从而实现不同的浸润性表面。飞秒激光微加工已经成功用于高质量、高精度的表面微纳加工,如钻孔、切割、纳米光栅、表面图案和纹理、纳米孔结构等[65-66]。

通过飞秒激光的直接烧蚀,可以在各种材料表面直接产生分层的微纳米尺度结构。并且,激光的加工位置、扫描速度、扫描轨迹可由程序精确控制,因此无需掩膜即可方便地设计和制作各种二维图案和三维微结构。近年来,飞秒激光微加工技术已经成功地应用于固体材料表面科学,通过调控激光和加工参数,调控固体材料表面微结构,能够实现不同的极端浸润性表面[67-68]。

2 飞秒激光制备耐久性超疏水表面

不同的应用场景下需要的超疏水表面也不尽相同,所对应的耐久性需求也有所差别。第1节已经介绍了飞秒激光微纳加工技术的特点,利用这些独特的优势,飞秒激光微纳加工技术在制备耐久型超疏水表面领域有很大的应用前景。根据基体材料本身的属性,利用飞秒激光微纳制造的特点在基体材料表面构筑精细微纳结构,再根据需要辅以其他制备方法,就可能在基体材料表面上制备出耐久型超疏水表面,图3简要概括了其中的关系。这里将超疏水表面基体材料大致分为聚合物、玻璃和金属,分类描述了利用飞秒激光制备对应耐久型超疏水表面研究现状。

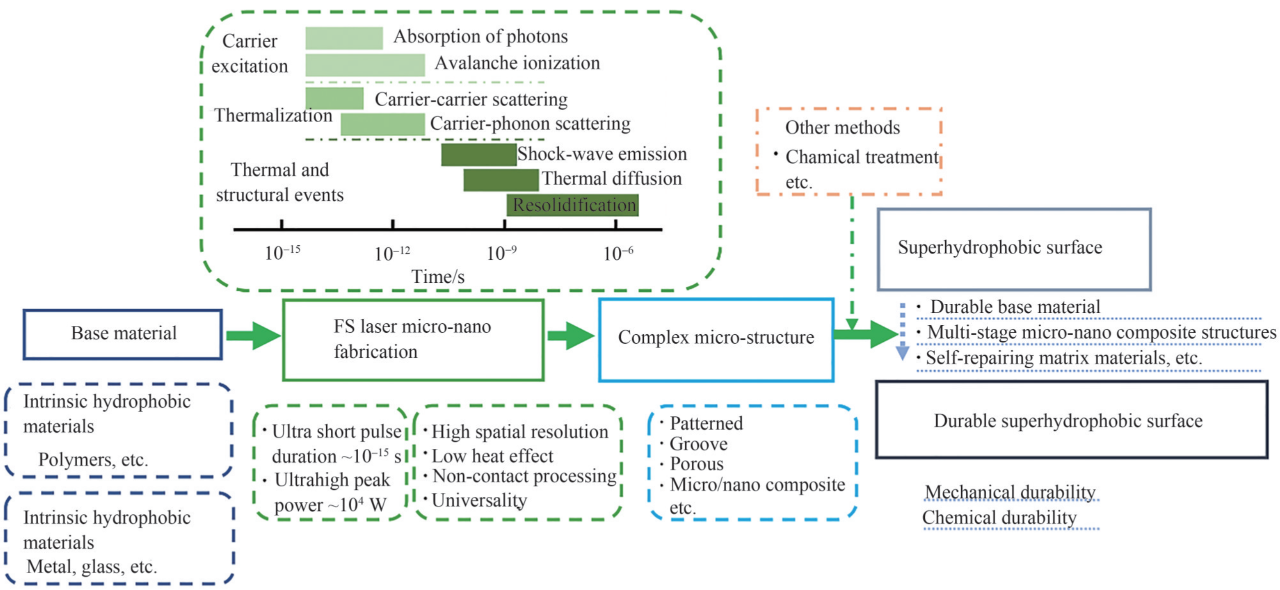


图3 飞秒激光制备耐久型超疏水表面

Fig. 3 Fabrication of durable superhydrophobic surface by femtosecond laser

2.1 聚合物

聚合物作为一种用途广泛的材料,在众多领域都有重要应用。聚二甲基硅氧烷(Polydimethylsiloxane, PDMS)具有柔韧性好、热稳定性好、光学透明度高、无毒、生物相容性好等特点[69]。此外,它也是一种常见的疏水基底。YONG J等利用一步飞秒激光烧蚀技术制备了各种超疏水PDMS表面[70-71]。聚焦飞秒激光在

PDMS表面可诱导形成微槽，大量不规则的纳米粒子随机地覆盖在微沟槽的壁和边缘。随着微槽相互靠近、重叠，出现了新的均匀的粗糙组织，表现为珊瑚状微观结构（图4）。珊瑚状结构的大小约为几微米，表面呈不规则、均匀分布的纳米突起，形成层次结构。该结构表现出很好地超疏水性（接触角157.5°）以及很低的液滴粘附性（滚动角1°）。因此，即使不进行任何改性，粗糙的PDMS表面也表现出超低的粘接超疏水性，这是因为激光诱导的微观结构捕获了大量空气，形成空气层，从而降低了水滴与PDMS的接触面积，赋予表面超疏水性。

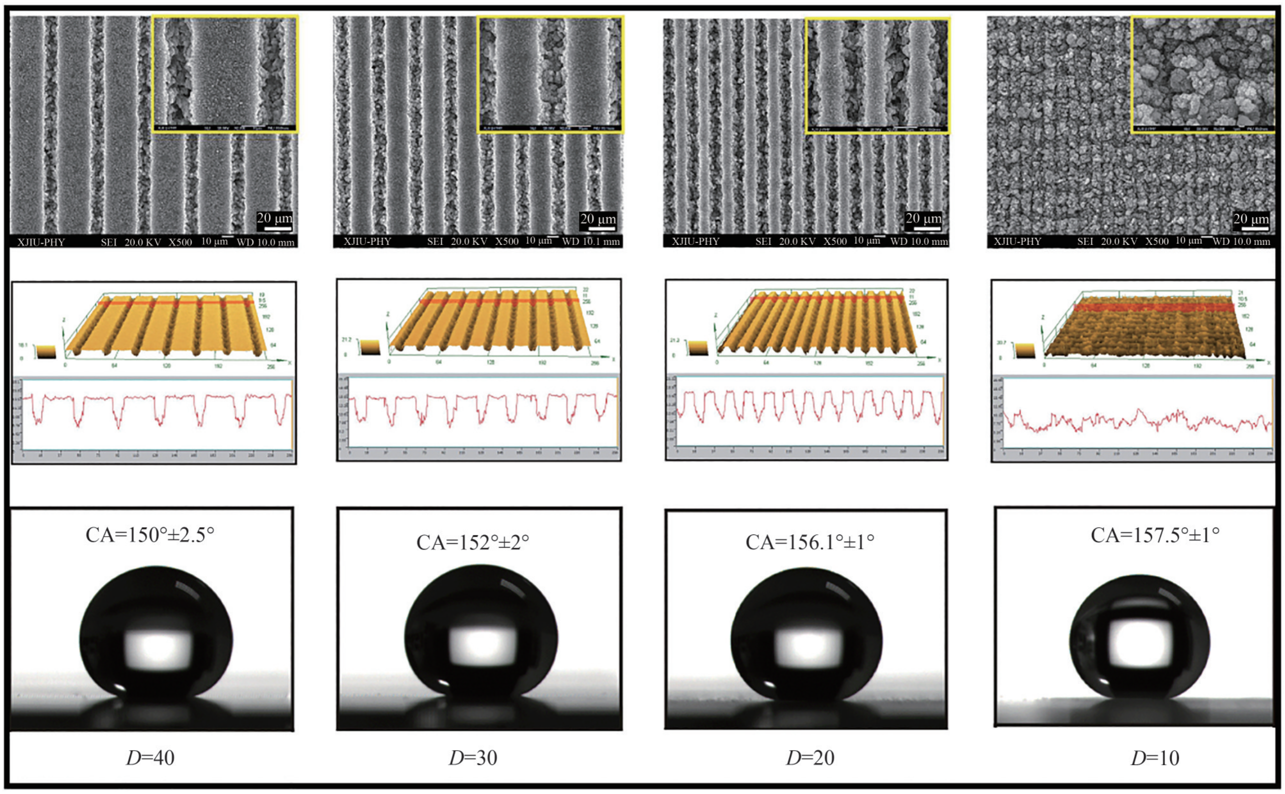
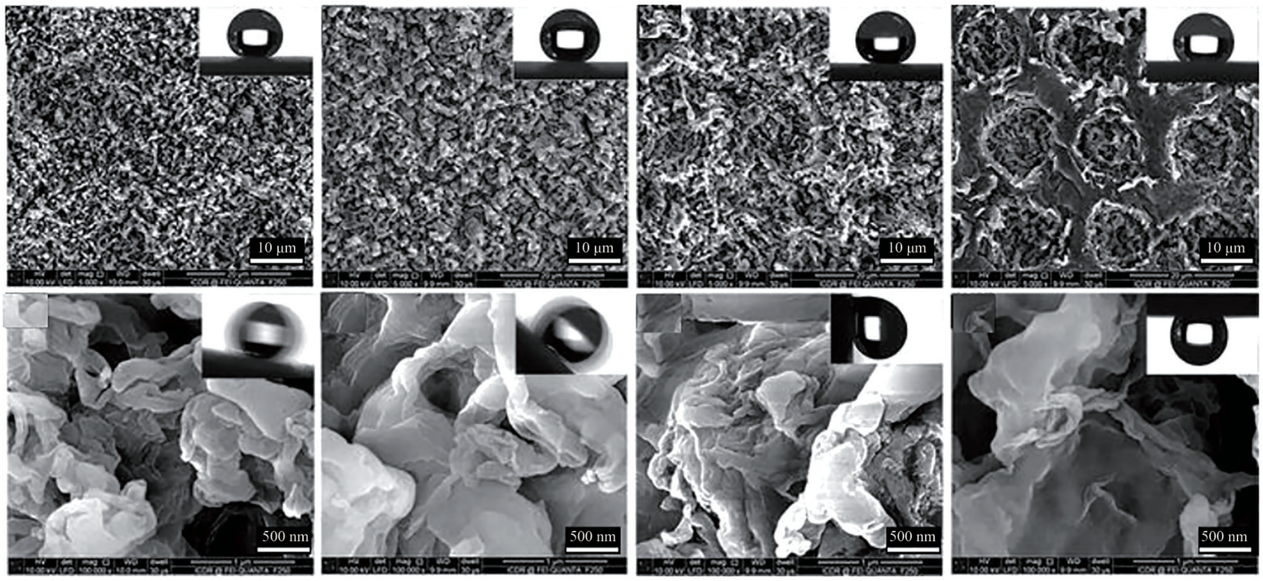


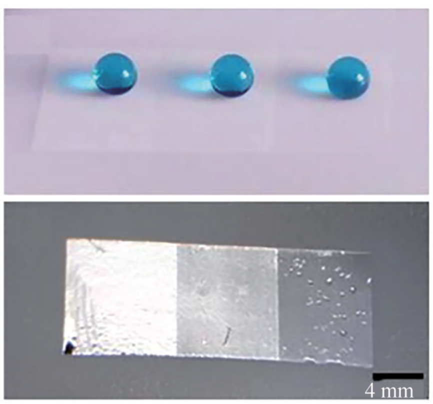
图4 飞秒激光加工PDMS表面不同间距微槽及纳米结构形貌，以及对应的接触角[70]

Fig. 4 Morphology of microgrooves and nanostructures with different spacings on PDMS surface and corresponding contact angles processed by femtosecond laser[70]

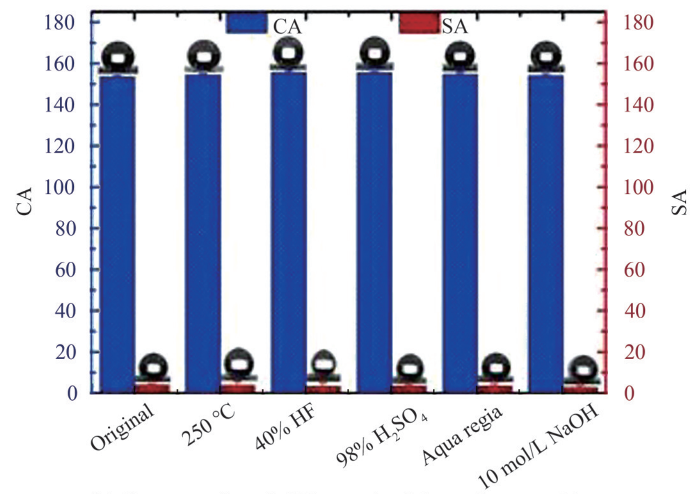
聚四氟乙烯（Polytetrafluoroethene，PTFE）由于成本低、耐化学性强、环境稳定等优点，被广泛应用于众多工业领域。PTFE基板能够在诸多恶劣环境，如强酸强碱溶液、极低或高温（−180 ℃～+250 ℃）甚至有机溶剂下长期贮存，而其表面形貌和化学成分几乎不发生变化。但这种优异的稳定性也为加工带来了许多困难。许多传统方法（如化学蚀刻、热处理、涂层、模板复制）都不适合在PTFE表面实现超疏水性，因为这些方法不能使PTFE基板粗糙化。然而，使用飞秒激光烧蚀技术能够直接在PTFE基板上构建微/纳米尺度的结构。YONG J等通过一步飞秒激光处理获得了超疏水PTFE表面[72]。经过飞秒激光烧蚀以后，PTFE表面形成了大量互相连接的气孔和突出物，由于PTFE材料属于本征疏水材料，由飞秒激光烧蚀的粗糙表面极大地增大了材料的比表面积，液滴在其表面时为Cassie状态，接触面积大大减小。图5（a）为飞秒激光烧蚀制备的PTFE微观结构及对应的接触角和滚动状态，CA为155.5°，SA为2.5°，图5（b）为液滴在加工的PTFE表面状态和PTFE样品，也体现了出了其优异的超疏水性能。此外，PTFE的化学稳定性优势确保了激光烧蚀PTFE表面超疏水性的耐久性。将PH值为1～13的水滴置于粗糙的PTFE板上，无论是酸性水滴还是碱性水滴，测得的CA均大于150°，SA小于10°。另外，飞秒激光制备的PTFE超疏水表面在各种恶劣环境中，包括高温（250℃）、40%氢氟酸、浓硫酸、10 mol/L氢氧化钠溶液，甚至在王水中储存一天后，都能保持其超疏水性能（图5（c））。这种耐用性与PTFE固有的化学惰性和激光诱导的微观结构密切相关。化学惰性导致无论是表面化学成分还是形貌方面的损伤速度都很低。同时，由于粗糙的表面微结构能够显著减



(a) Surface morphology and wettability characterization after femtosecond laser ablation of PTFE



(b) Superhydrophobic PTFE and morphology of water droplets on its surface



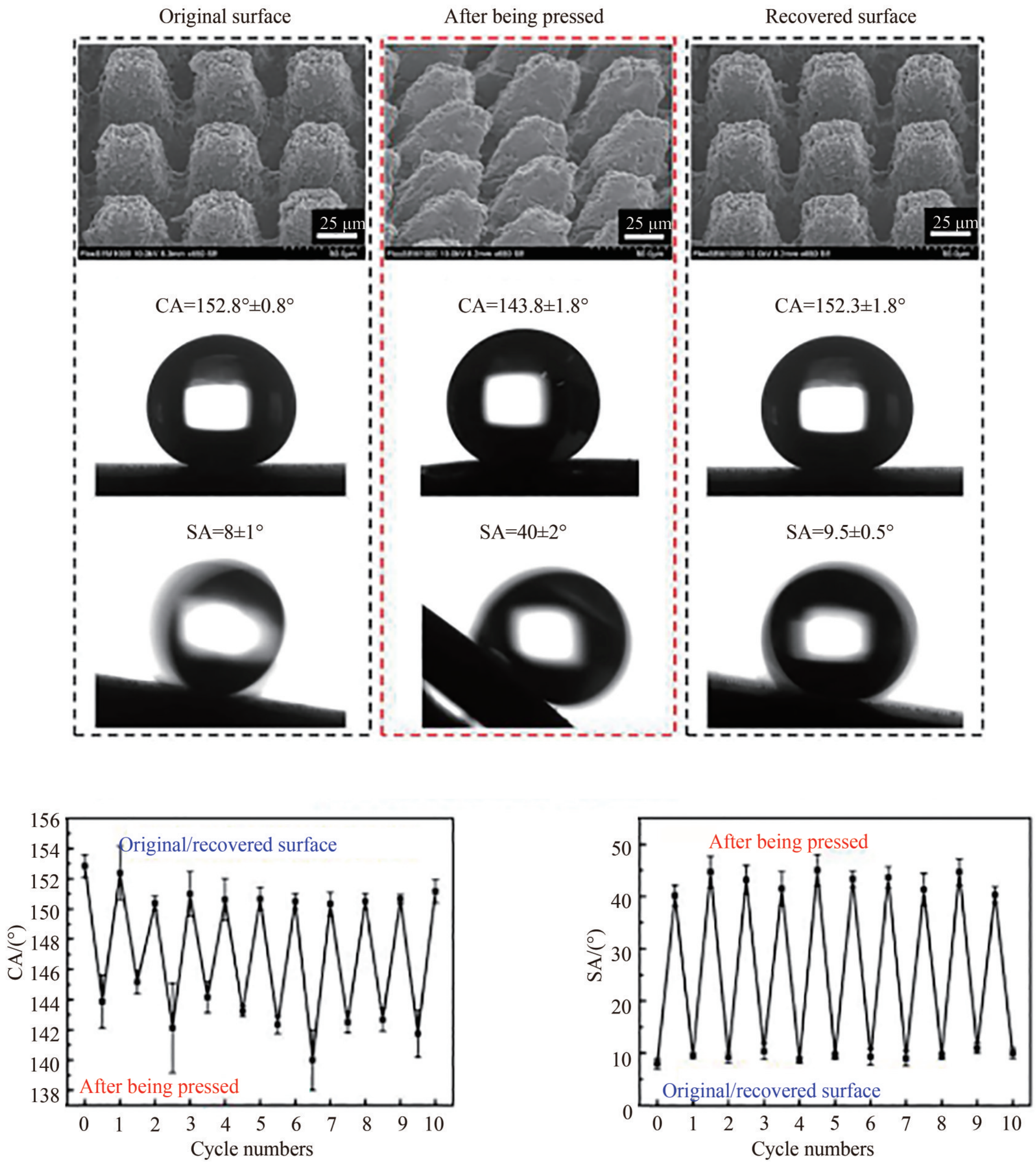
(c) Contact angle and sliding angle of the surface stored in different harsh environments for one day

图5 飞秒激光加工的PTFE耐久型超疏水表面[72]

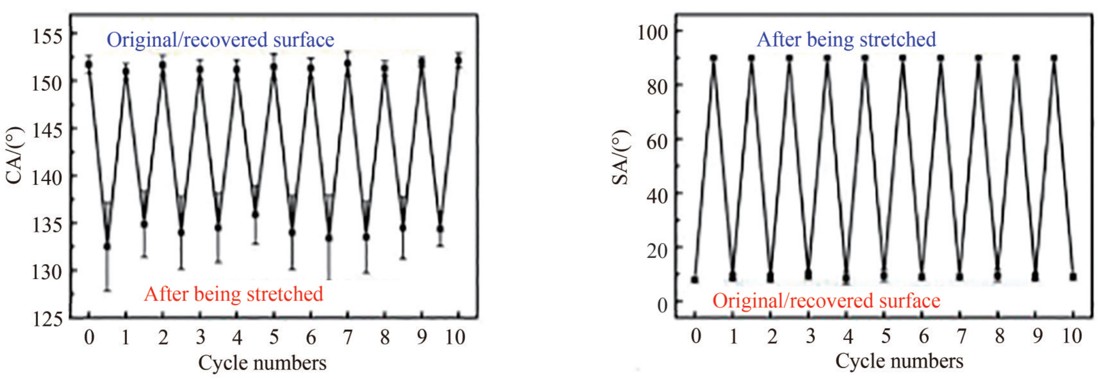
Fig. 5 PTFE durable superhydrophobic surface fabricated by femtosecond laser[72]

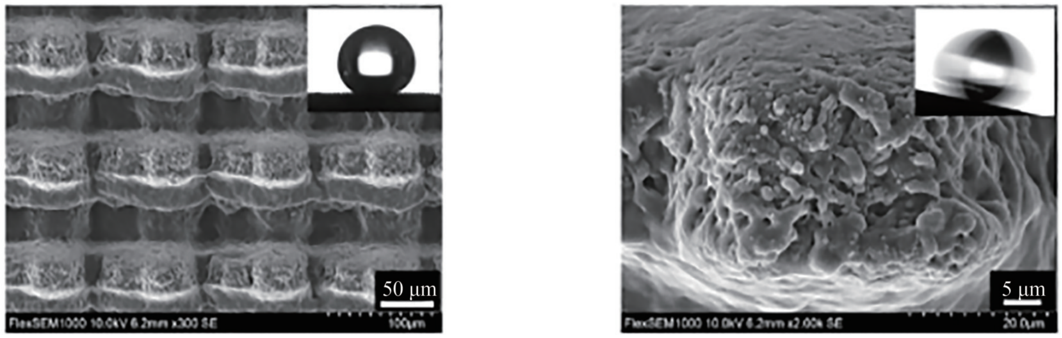
少腐蚀性液体和PTFE表面之间的接触面积，极大地增强了耐久性。

除了选择稳定的基体材料外，材料的自修复性能也会明显提高超疏水表面的耐久性。形状记忆聚合物（Shape Memory Polymer，SMP）是一种新型智能材料，具有独特的形状记忆特性，通过设计合适的微纳米结构可以在SMP表面实现可恢复超疏水表面[73-74]。最近，BAI X利用飞秒激光在石墨烯掺杂形状记忆聚合物（RGO-SMP）复合材料表面构建微柱阵列，并进一步制备了阳光驱动的可恢复超疏水表面[75]。原始RGO-SMP微柱的CA为152.8±0.8°，SA为8±1°，表现出低粘滞超疏水性。微柱阵列经过挤压或拉伸变形处理后，会使得表面失去超疏水性。但是由于材料本身优异的光热转换性能，在一个太阳光强度下其表面温度可以迅速升高并超过材料的形状转换温度（图6（a））。因此，RGO-SMP微柱的表面形貌和润湿性在阳光下能够完全恢复到原始状态。同时，这种可逆变形和恢复过程可以重复多次，且不降低表面的超疏水性（图6（b））。此外，该表面还具有优异的紫外耐久性和PH稳定性，在持续经受紫外线照射140小时后接触角始终保持在150°以上，在PH=2、4、6、8、10、12的溶液中分别浸泡72小时后，CA也都大于150°，表明了其优异的化学稳定性（图6（c））。

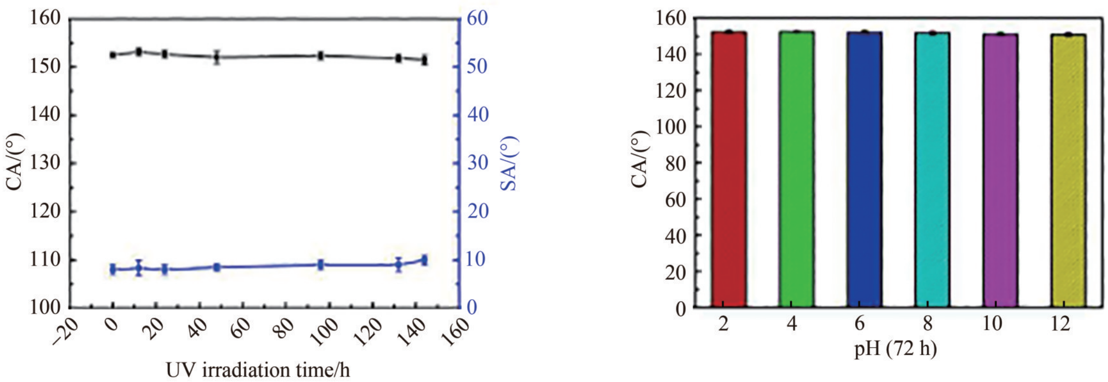


(a) Reversible changes in contact angle and sliding angle of RGO-SMP microcolumn arrays in the original state, pressed state and sunlight recovery state





(b) Surface morphology and wettability of RGO-SMP microcolumn arrays recovered after 10 times stretching and sunlight irradiation



(c) Stability of RGO-SMP microcolumn arrays in ultraviolet radiation and different pH solutions

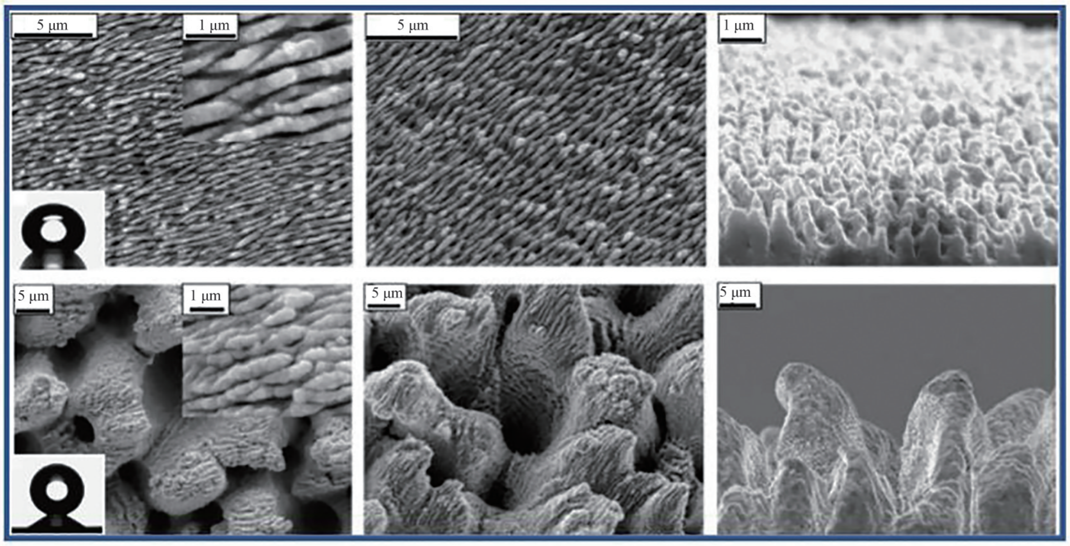
图6 耐久型RGO-SMP超疏水表面[75]

Fig. 6 Durable RGO-SMP superhydrophobic surface[75]

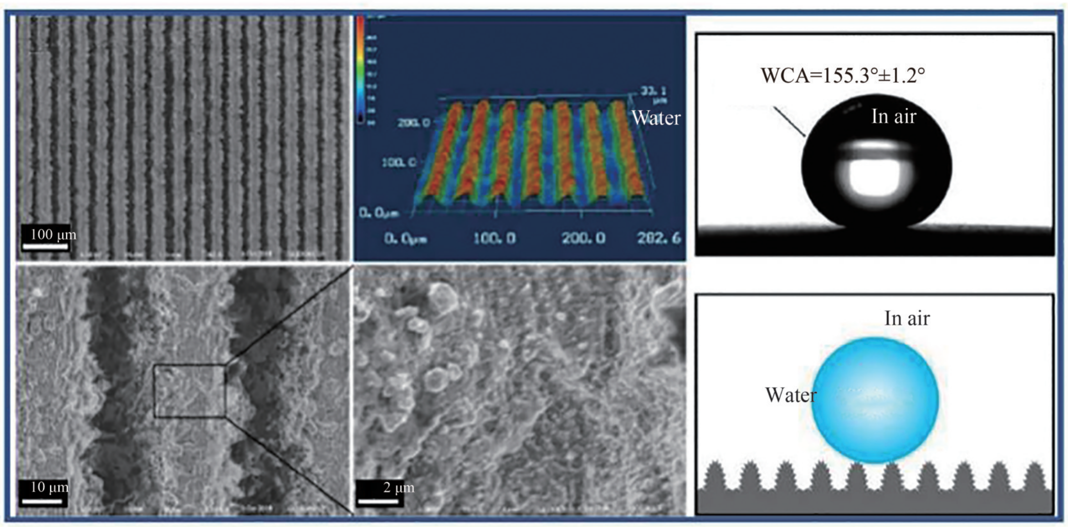
2.2 金属

金属材料广泛应用于日常生活、工业、农业生产中,如建筑、汽车、机器、绳索、飞机、船舶等。但金属类设备通常会受到污染、腐蚀、生锈、氧化、结冰等问题的困扰。这些困扰会造成巨大的经济损失甚至引发更严重的事故[76]。赋予金属表面超疏水性是解决上述问题的有效途径[77]。KIETZIG A等利用飞秒激光烧蚀在不同的金属合金上制备了特定的粗糙双尺度微观结构[78]。将处理过的表面在空气中储存30天,这些表面的浸润性将从超亲水性转变为超疏水性,因为激光诱导的微观结构极大地增大了比表面积,从而倾向于吸收大气中的含碳化合物,降低了表面能。

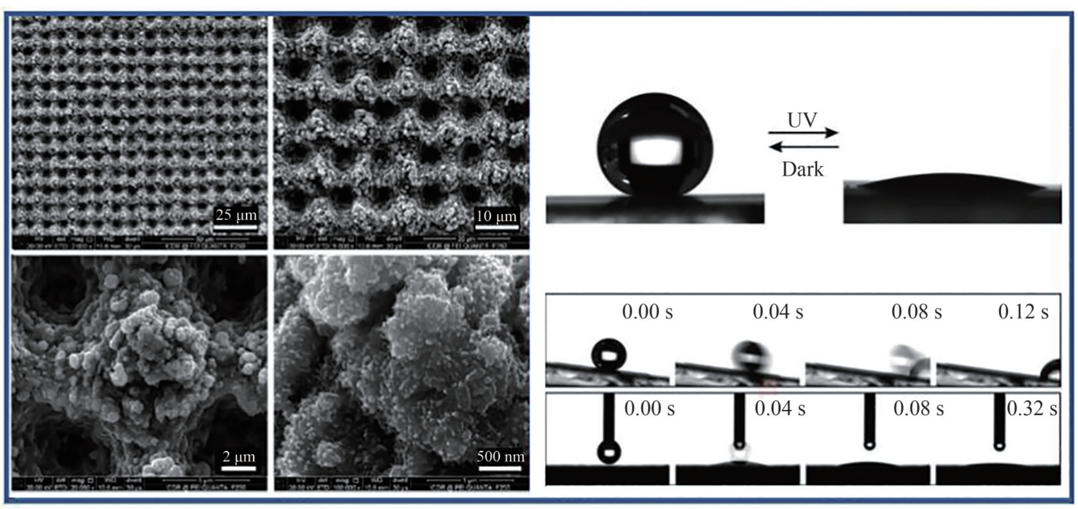
WU B等使用飞秒激光在不同的激光能量下烧蚀不锈钢并制备了超疏水表面[79]。在真空环境中,激光聚焦于样品表面进行烧蚀形成周期性的纳米结构,称为激光诱导周期性表面结构(Laser-Induced Periodic Surface Structures,LIPSS)。LIPSS的方向垂直于激光束的偏振方向,是激光辐照所特有的一种性质,通常由入射激光脉冲与先前脉冲产生的散射切向波之间的干涉引起[62]。随着激光能量的增加,产生了比LIPSS更宽的分离突起,分离的突起变成几微米大小的锥形尖峰(图7(a))。尖峰的顶部也被典型的LIPSS覆盖,形成分层的微米和纳米级结构。用硅烷试剂对不同样品表面进行低表面能处理后,具有分层微纳米结构的表面表现出超疏水性和对水滴的极低粘附,CA为166.3°,SA为4.2°。YONG J等利用飞秒激光在Al、Zn等金属上制备出了超疏水表面[80-81]。其中,在Al表面,烧蚀出具有微纳米结构的沟槽,经过低表面能物质修饰后,展现出明显的超疏水功能(图7(b))。通过擦除低表面能物质,能够切换其润湿性性质。在Zn表面加工制备了可切换润湿性的超疏水表面,图7(c)为飞秒激光烧蚀后样品表面形貌,为典型的微纳米级分层结构。均匀的微山结构排列在Zn表面,每座微山结构的表面也覆盖着大量不规则的纳米突起。未处理的表面,由锌原子比例为100%的锌元素组成。激光烧蚀后,样品表面Zn的原子比例下降到67.56%,出现了新的元素O,其原子比例为32.44%。结果表明,飞秒激光处理过程中也发生了氧化,导致原始Zn基板上出现了一层薄而粗糙的ZnO层。粗晶ZnO微结构在暗储存后表现出超疏水性,测得的CA和SA分别为159.5°和8°。通



(a) Microstructure and corresponding contact angle of stainless steel surface ablated by femtosecond laser under different laser fluxes



(b) SEM images and three-dimensional profile of Al surface processed by femtosecond laser



(c) Microstructure of Zn surface after femtosecond laser treatment, and contact angle changes under dark static and ultraviolet irradiation

图7 飞秒激光在不同金属基体上制备超疏水表面[79-81]

Fig. 7 Superhydrophobic surfaces prepared by femtosecond laser on different metal substrates[79-81]

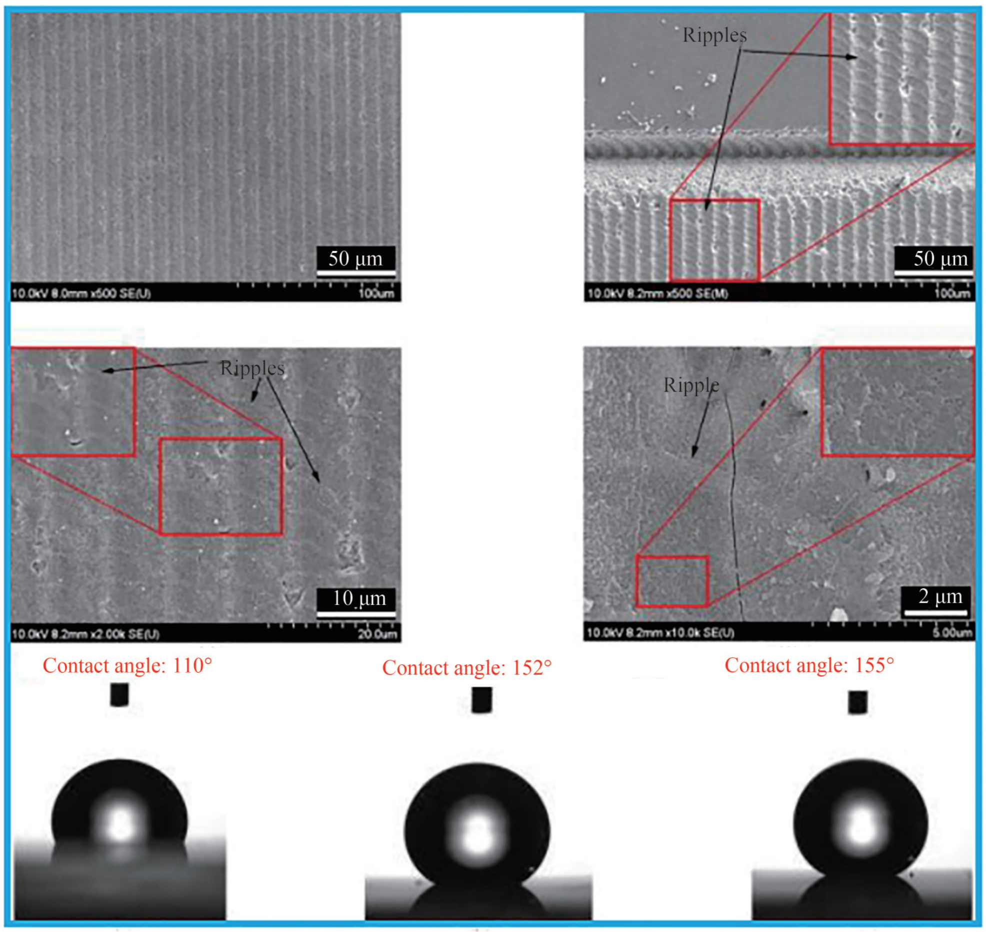
过交替的紫外照射和暗储存，表面能够在超疏水性和准超疏水性之间可逆切换。

2.3 玻璃

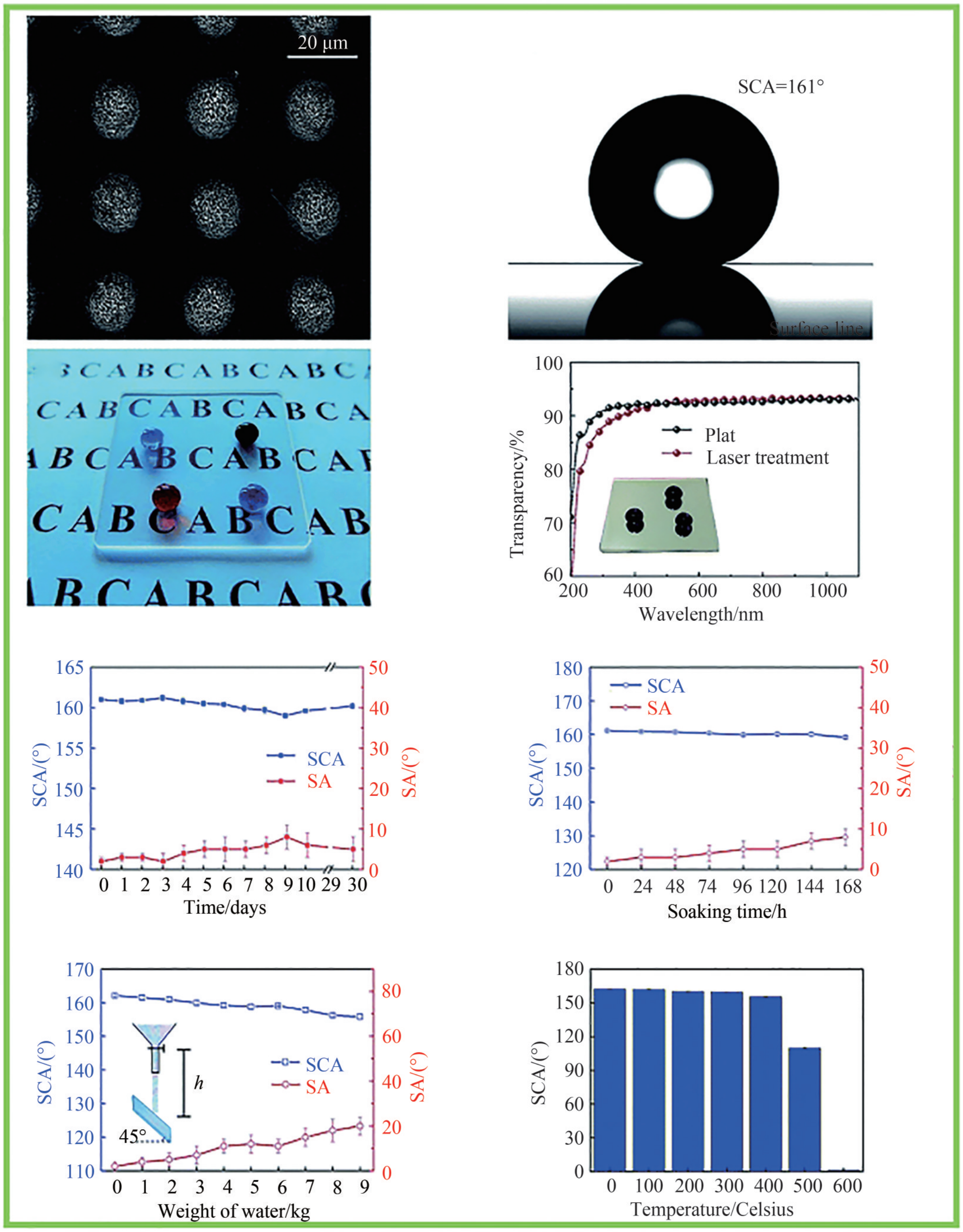
玻璃由于其极高的硬脆度，是一种典型的难加工材料，而利用飞秒激光则很容易在玻璃表面加工出微纳米结构。ZHOU M等利用飞秒激光在K9玻璃表面构建了一种双尺度结构[82]。通过对样品表面进行多次激光扫描形成微沟槽，微沟槽中还存在大量规则的亚微米结构（图8(a)）。通过氟硅烷改性降低了双尺度粗糙结构的表面自由能，得到的玻璃表面表现出明显的超疏水性。水滴的CA和SA分别为152.3°和4.6°。相比之下，硅烷化光滑的K9玻璃上的水滴的CA仅为114.7°。AHSAN M等也通过飞秒激光微加工方法在钠-石灰玻璃表面实现了超疏水性[83]。激光扫描在玻璃表面形成周期为10 μm的微光栅（图8(b)）。每条轨迹都被激光束烧蚀了两次。周期微光栅宽度为8 μm。同时还形成了宽度为2 μm的微柱作为相邻微栅的边界。微光栅底部存在周期性的自组装微波纹和不均匀的纳米结构。该微纳结构玻璃表面经氟烷基硅烷进一步化学处理后，其CA在152°～155°之间。

LIN Y等利用飞秒激光在硅玻璃表面直接诱导出微坑阵列，制备了透明的超疏水表面[84]。图8(c)显示

(a) The morphology and contact angle of the K9 glass surface ablated by femtosecond laser and the smooth K9 glass surface



(b) Micro-grating morphology and contact angle formed by femtosecond laser on glass surface



(c) Micropit arrays induced on glass, superhydrophobic characterization and durability characterization

图8　飞秒激光在玻璃表面制备的耐久型超疏水表面[82-84]

Fig. 8　Durable superhydrophobic surface prepared by femtosecond laser on glass surface[82-84]

了激光诱导微坑的微观结构，微坑呈均匀、周期性排列。微坑的内表面呈亚微米波纹状，波纹结构上还形成了大量的纳米棒和纳米颗粒。经过化学修饰降低表面自由能后，微纳米结构玻璃表面表现出优异的超疏水性能，CA为161°，SA为2.1°。并且，分层微坑对玻璃的透光率影响极低。超疏水玻璃在可见光和近红外波段的透明度均高于92%。同时所制备的超疏水表面有出色的耐久性，在空气中放置一个月，在水中浸泡一周，表面的接触角和滚动角变化很小（CA>155°，SA<10°），9 kg的水流持续冲击表面后，仍然保持优越的超疏水性能和透明度。利用落砂试验表征了表面的耐磨性能，粒径从100 mm到300 mm的砂子从20 cm高处以30 g·min^{-1}速度对表面进行冲击，持续5 min后接触角仍然大于155°。所制备的表面还有出色的热稳定性，试样在管式炉中保存1小时，温度从100℃升到500℃时接触角均大于150°（图8(c)）。

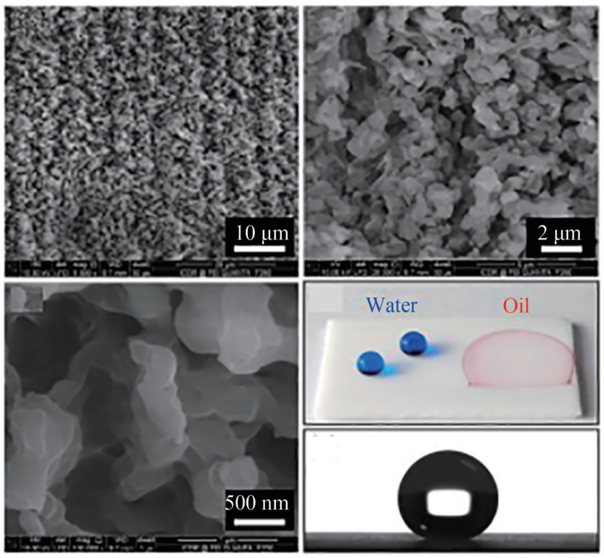
3 应用

3.1 自清洁

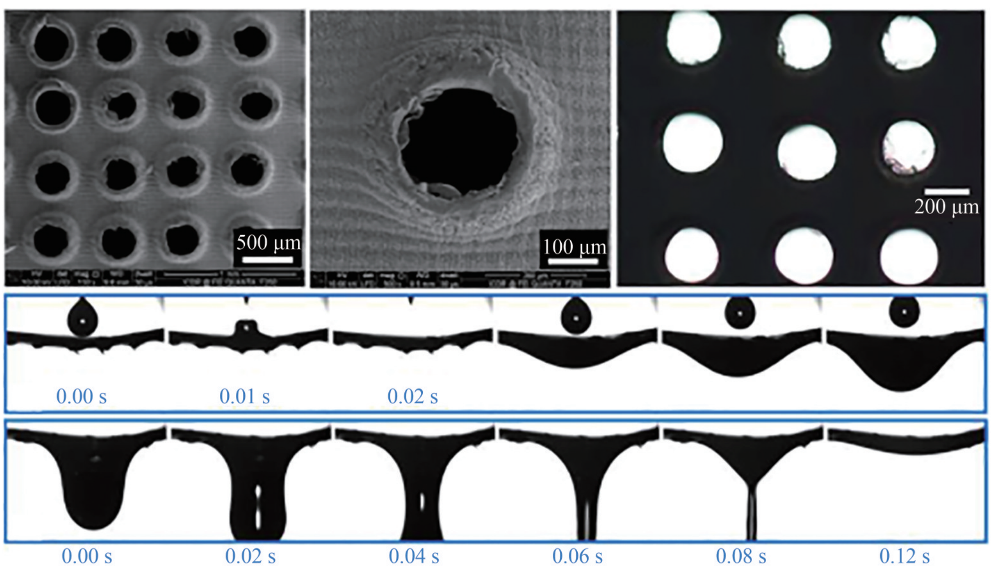
与荷叶一样,飞秒激光诱导的人工超疏水表面也具有良好的自清洁能力[70]。当超疏水表面被固体尘埃颗粒污染时,落在样品表面的水滴(如雨滴)将自由滚动并收集其路径上的所有尘埃颗粒。与普通光滑表面相比,超疏水表面上的水滴保持准球形且容易滚落。因为水比固体表面对大多数灰尘有更强的亲和力,在滚压过程中,水滴可以吸附外来的灰尘颗粒。自洁功能使人工超疏水材料可以应用于室外建筑、汽车外壳、手机屏幕、太阳能电池板等领域。

3.2 油水分离

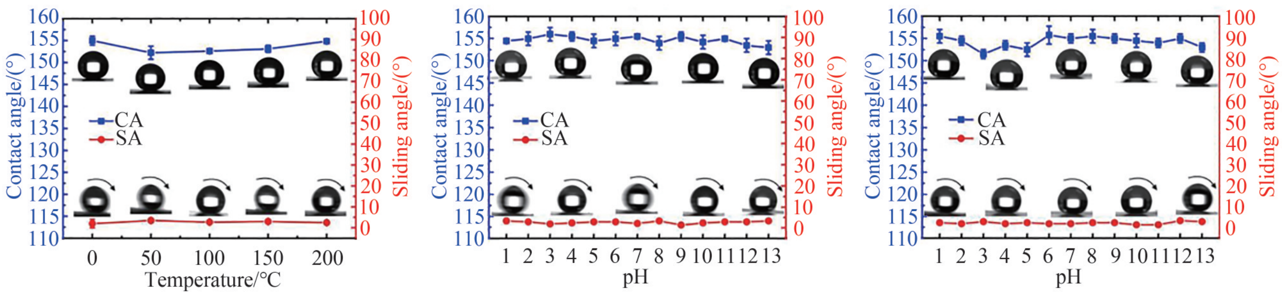
频繁的漏油事故和含油工业废水的排放,造成了巨大的经济损失,并严重污染了自然生态环境[85-86]。CHEN F 等提出了一种利用飞秒激光结构超疏水多孔聚四氟乙烯薄片分离油水混合物的方法[87]。首先使用飞秒激光对聚四氟乙烯薄片表面进行烧蚀,在薄片上形成分层微结构,从而制备成超疏水聚四氟乙烯表面(图 9(a))。在此基础上,使用机械钻孔在表面上形成一系列的微孔,所制备的多孔试样在具有出色的超疏水性能的同时,油可以彻底湿润薄片表面,并通过微孔渗透。当将水和油的混合物倒在超疏水超亲油多



(a) Morphology of PTFE surface ablated by femtosecond laser and wettability characterization of water droplets and oil droplets



(b) SEM images and optical microscope photographs of PTFE sheet with microporous array structure, the process of oil droplets penetrating into PTFE membrane



(c) Durability of superhydrophobic PTFE surface induced by femtosecond laser. wettability of samples stored at different temperatures for one day, wettability of samples soaked in different pH solutions, wettability of samples soaked in different pH solutions for one day

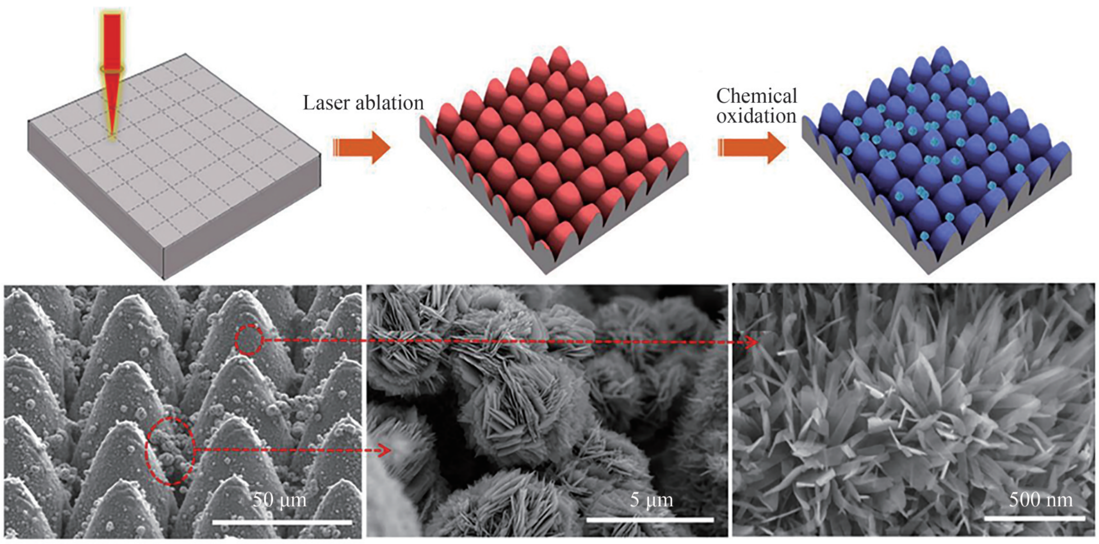
图9 飞秒激光加工的耐久型超疏水PTFE表面油水分离应用[87]

Fig 9 Application of oil-water separation on durable superhydrophobic PTFE surface processed by femtosecond laser[87]

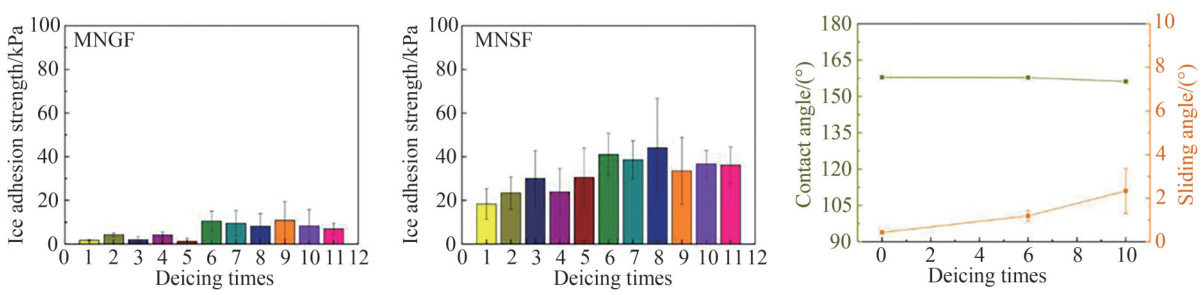
孔板上时，超亲油性使油相液体能够穿透并穿过多孔板，而超疏水性使得薄片能够截留水分。最后，将油水混合物成功分离为试样上方的水部分和试样下方的油部分（图9(b)）。激光烧蚀聚四氟乙烯的超疏水性耐久性优异，所制备的样品在不同温度、不同酸碱溶液中都能够保持其超疏水性能，在不同酸碱性溶液中浸泡一天还拥有出色的超疏水性能（图9(c)），这些优异的耐久性使得超疏水性多孔聚四氟乙烯甚至可以分离油类和强酸/强碱溶液的混合物。

3.3 防冰

PAN R等设计了一种三重尺度的超疏水微结构，具有抗冰性能[88]。飞秒激光烧蚀结合化学氧化在铜片上产生周期性的分层微锥，微锥表面覆盖着纳米草和微花（图10(a)）。在Cassie状态下，表面表现出稳定的超疏水性能，临界拉普拉斯压力可达1 450 Pa。超疏水表面具有良好的防结冰能力，这主要归功于冲击液滴



(a) Laser preparation steps and surface morphology of triple-scale micro/nano structured superhydrophobic surfaces



(b) Ice stability test results of superhydrophobic surfaces

图10 超疏水表面的抗冰应用[88]

Fig. 10 Anti-ice of superhydrophobic surface[88]

的快速滚落、层叠冷凝的抗湿性以及冻结条件下固液界面非均相成核的显著延迟。当液滴撞击超疏水表面时，液滴可以反弹20多次以上。液滴与样品表面接触时间小于9 ms，避免了液体与固体表面的完全接触。在高湿条件下，微锥间凝聚的二次微滴可以向上移动，并不断被凝聚的一次微滴吸收，因此表面微观结构之间的空间充满了空气，而不是凝聚的微滴。被困在表面微结构中的空气就像一个热阻层，可以显著减少固体表面与液体之间的传热。Cassie状态下稳定的空气层导致固液界面处的非均相形核显著延迟。此外，冰在超疏水表面的粘附强度仅为1.7 kPa，冰块甚至可以凭借自身重量滑落，并且此过程能够重复多次（图10(b)）。因此，所制备的超疏水表面不但具有防结冰性，还具有优异的疏冰性能。

4 结论

超疏水表面在油水分离、防结冰和自清洁等领域具有巨大的潜力，但在实际应用中却受到较大限制。对于超疏水表面，其表面结构的脆弱是阻碍其实际应用的主要原因。由于对超疏水表面研究的不断深入，超疏水表面失效的原因也得到了探索。本文综述了飞秒激光制备耐久型超疏水表面及其应用的研究进展。文章从润湿性的几个基本模型出发，首先分析了耐久型超疏水表面的特点，介绍了飞秒激光微纳加工在超疏水表面制备的优势。从聚合物、金属、玻璃等不同材料介绍了飞秒激光制备耐久型超疏水表面的研究进展，随后对耐久型超疏水表面应用的领域进行了概述。

飞秒激光微纳加工在制备耐久型超疏水表面具有诸多优点，展现出了巨大的应用前景，但是在面临实际应用时仍然存在挑战。1)飞秒激光加工系统目前大多处于实验室阶段，加工面积有限，在大面积加工方面还需进一步的发展。2)所制备超疏水材料的耐久性与基体材料的性质紧密相关，若基体材料耐久性好，则所制备的超疏水表面耐久性就好；若基体材料耐久性一般，则所制备的超疏水表面耐久性也表现一般。3)金属、玻璃材料基体大多为本征亲水表面，制备超疏水表面时需辅以低表面能化学处理，而低表面能物质一般附着在表面微纳结构上，增强其结合力也是其超疏水表面保持耐久性所面临挑战。

随着对超疏水表面研究的不断深入，超疏水表面失效的原因也得到了探索。利用飞秒激光微纳加工技术制备耐久型超疏水表面，使其能够具有实际应用的价值，可以从几个方面入手：1)配合使用大面积的移动加工平台，以用来加工大面积的样品。2)根据应用需要，选择耐久性良好的基体材料，结合超疏水表面失效的特点，还可以与其他手段进行结合，例如化学修饰、电化学沉积等方法进行多尺度微纳结构的构筑，增强表面粗糙结构的耐久性。3)对于本征亲水的基体材料，可以通过其他手段增强低表面能物质与基体材料的结合，比如粘合剂、二次加工等方式。依托飞秒激光微纳加工的优势，再结合其他的制备方法，有望在许多材料上制备出耐久型超疏水表面，这也极大拓展了耐久型超疏水表面在自清洁、油水分离以及抗冰等领域的应用前景。

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Research Progress of Femtosecond Laser Preparation of Durable Superhydrophobic Surface and Its Application (Invited)

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Abstract: Although superhydrophobic surfaces have shown great potential in oil-water separation, anti-icing and self-cleaning, the practical applications were often limited by their brittle durability. The fragility of superhydrophobic surface structure is the main reason that hinders its practical application. Due to the further study of superhydrophobic surface, the failure of superhydrophobic surface has also been explored. This paper reviews the research progress of durable superhydrophobic surface prepared femtosecond laser and its application.

In the section of background, firstly, several basic wettability models are introduced, and the characteristics of durable superhydrophobic surfaces are analyzed. Then, the advantages of femtosecond laser micro-nano processing in the preparation of superhydrophobic surfaces are discussed. The research progress of femtosecond laser preparation of the durable superhydrophobic surface for different materials such as polymer, metal and glass were concluded. The application fields of durable superhydrophobic surface fabricated by femtosecond laser were summarized.

There are several methods to improve the durability of the superhydrophobic surface according to the application requirements. Firstly, the mechanical stability of the superhydrophobic surface with multi-scale micro-nanocomposite structure is much higher than that of the single micron or nano-scale rough structure. Secondly, the durability of superhydrophobic surface can also be improved by strengthening the surface microstructure on the material surface through the bonding layer. This form of adhesive can not only strengthen the bonding strength between microstructure and surface, but also play a buffer role when the surface is impacted by external force, protecting the micro-nano rough structure, and effectively improving the mechanical durability of superhydrophobic surface. Thirdly, the physical protection of micro-nano structures is carried out by constructing a surface protective layer, thereby improving their mechanical durability. Finally, the construction of self-healing superhydrophobic surface has become a powerful mean to improve the durability. Different from the previous strategies, self-healing strategies mainly focus on the recovery of damaged superhydrophobic function, thereby extending its service life. Finally, the matrix material with good intrinsic durability can be selected. Combined with femtosecond laser, a durable superhydrophobic surface can be prepared. Considering the failure reason of superhydrophobic surface and the advantages of femtosecond laser processing, durable superhydrophobic surfaces were prepared on different durable matrix materials, which is of great significance to the practical application of superhydrophobic surfaces. The variety of application requirements of superhydrophobic surfaces are different, and the corresponding durability requirements also show a great variety. Regarding the matrix materials, the superhydrophobic surface matrix material can be roughly divided into polymer, glass and metal. In terms of polymers, the superhydrophobic surface with excellent durability in PTFE can be easily prepared by femtosecond laser, as PTFE is in great stability. Besides, femtosecond laser can also prepare light responsive superhydrophobic surface on shape memory polymer. After the surface structure is deformed by an external force, it can recover to the initial state under a sunlight, and then restore to the superhydrophobic state. For metal materials, femtosecond laser combined with low surface energy material modification can directly prepare superhydrophobic surfaces on stainless steel, aluminum, zinc and other metal surfaces, and some of the superhydrophobic properties will change interestingly. For example, superhydrophobic surfaces fabricated on zinc can change the superhydrophobic properties in UV irradiation and dark storage. In terms of glass, the prepared superhydrophobic surface has very good mechanical stability and thermal stability. Based on the properties of the substrate material, adjusting the femtosecond laser processing strategy and parameters, and then implementing appropriate chemical modification according to the needs, can give the surface of the substrate material superhydrophobic properties.

Generally speaking, the durability of superhydrophobic surface includes mechanical durability and chemical durability. To improve the mechanical durability, multi-scale micro-nano structures need to be constructed. The femtosecond laser has great advantages in constructing multi-scale micro-nano structures, which can be applied to almost all hard materials. In terms of chemical durability, femtosecond laser also achieves very stable superhydrophobic surfaces on some chemically stable and difficult-to-machine materials. Based on many different matrix materials, superhydrophobic materials have been increasingly applied in many fields such as self-cleaning, oil-water separation and anti-icing. Superhydrophobic materials have been applied in real life in the field of self-cleaning, chemical stability, as well as anti-ultraviolet. In oil-water separation, due to the excellent durability of matrix materials, the durable superhydrophobic materials play a huge role in solving oil pollution and industrial wastewater treatment. As for anti-icing, due to the low ice adhesion and mechanical durability in superhydrophobic materials, the key problems of transportation and aviation are hopeful to be solved.

With the advantages of high machining accuracy, good universality and strong controllability of femtosecond laser in the field of micro-nano processing, supplemented by other methods such as chemical modification, and combined with the failure characteristics of superhydrophobic surfaces, it is expected to prepare durable superhydrophobic surfaces on many materials, which also greatly expands the application prospect of durable superhydrophobic surfaces in the fields of self-cleaning, oil-water separation and antiicing.

Key words: Durability; Superhydrophobic; Femtosecond laser; Oil-water separation; Anti-icing

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