

Progress on the Fabrication of Rough Surface for Superhydrophobicity and Its Application

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Received: Mar. 20th, 2018; accepted: Apr. 30th, 2018; published: May 7th, 2018

Abstract

The superhydrophobic surface has attracted attentions in the field of industry and scientific research due to its features such as self-cleaning, drag reduction and dust-repellent properties. This article reviews the progress on the preparation of rough surface for superhydrophobicity and its application. Meanwhile, the disadvantages of superhydrophobic surfaces are evaluated and their development directions are discussed.

Keywords

Superhydrophobic Surface, Micro and Nano Structures, Rough Surface

超疏水表面粗糙结构的构造及其应用研究进展

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收稿日期: 2018年3月20日; 录用日期: 2018年4月30日; 发布日期: 2018年5月7日

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摘要

超疏水表面具有自清洁、减阻、防尘等多种特性,在生产生活及科研领域备受瞩目。本文综述了超疏水表面制备方法的研究进展及其在不同领域的应用进展。最后简要讨论了超疏水表面存在的不足,并对其发展方向进行了展望。

关键词

超疏水表面, 微纳结构, 表面粗糙结构

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1. 引言

在雨水、日照或风吹等自然外力作用下即可自动清除或降解表面污垢灰尘的自清洁表面自问世以来即受到广泛关注。过去的十几年中,受荷叶效应的启发,拥有超疏水特性的自清洁表面成为了发展的主流[1] [2] [3] [4]。超疏水材料依靠在表面构建微纳结构从而获得稳定的气-液层(Cassie-Baxter体系)[5],使得水滴无法附着。一般来说,超疏水表面通常指水接触角大于 150° ,同时滚动角小于 10° 的表面[6]。

自二十世纪九十年代中期以来,超疏水一直是一个活跃的科研领域。一般来说,适用于微米结构和纳米结构构造的技术如光刻、化学刻蚀、沉积和自组装等,都已经被广泛应用于超疏水表面粗糙结构的构造(表1)。尤为有趣的是,通过结合荷叶效应与X射线辐射、动态效应、光学效应[6] [7] [8] [9]等方式,超疏水表面可以直接由亲水材质表面改性得到。

获得超疏水表面的两个主要关键因素是低表面能及合适的粗糙度[1]。基于此,超疏水表面的制备方法也分为两种:第一,将原本就疏水的材料通过构造粗糙表面得到超疏水性能;第二,通过降低粗糙的亲水表面的表面能或在其上施加疏水材料来得到超疏水特性[10]。值得注意的是,粗糙度通常比低表面能更为关键,因为适度疏水和超疏水的材料在表面粗糙时都表现出相似的润湿行为。所以本文总结了粗糙度的构造方法,从刻蚀法、沉积法、铸造法等几个大类的最新研究进展进行了综述。

Table 1. Regular method for constructing a rough surface

表 1. 构造粗糙表面的一般方法

刻蚀法	形变法	沉积法	铸造法
光刻/X射线[11] [12] [13]	拉伸延展[20]	旋涂[21]	模板法[31] [32]
电化学腐蚀[14]		提拉浸渍[22]	打印法[33]
等离子体[15] [16]		化学气相沉积[23]	
化学刻蚀[17] [18]		蒸镀[24]	
电子束[19]		自组装[25] [26]	
		电镀[27]	
		喷涂[28] [29]	
		静电纺丝[30]	

2. 刻蚀法制备粗糙结构

在所有刻蚀法中, 光刻技术能够构建出最为均匀的粗糙结构, 一般用于创建大面积的周期性微/纳米结构。Bhushan 和 Jung [34]利用激光刻蚀在硅表面构建了均匀的微米阵列, 使表面达到疏水状态, 接着利用气相沉积法将 1,1-2,2-全氟十二烷基三氯硅烷(PF3)沉积在样品表面从而获得了一个接触角高达 170° 的超疏水表面。Martines 及其团队[35]利用电子束光刻技术制备出有序排列的纳米坑和纳米柱阵列, 组合成一个尖顶面状结构, 再使用十八烷基三氯硅烷(OTS)修饰后获得了静态接触角为 164° 、接触角滞后只有 1° 的超疏水表面。

Qian 和 Shen [17]通过简单的化学刻蚀法在金属基底构造出超疏水表面(见图 1)。首先, 对铝等多种金属进行位错选择性化学腐蚀, 再利用氟硅烷进行修饰, 最终, 被蚀刻的金属表面表现出了超疏水特性。

3. 形变法在制备粗糙结构

拉伸法也被用于制备超疏水表面。Zhang [36]及其团队通过拉伸聚四氟乙烯膜使其转变为在表面具有很多空隙的纤维状晶体, 从而使其表面粗糙度增大得到超疏水特性(如图 2)。

4. 沉积法制备粗糙结构

Shibuichi [37]等人将烷基乙烯酮二聚体(AKD)涂抹于玻璃板上, 使其自发在玻璃表面形成分形结构。在没有任何氟化处理的情况下, 他们获得了一个接触角大于 170° 的超疏水表面。Klein 及其团队[38]将基板简单的浸泡入含有纳米二氧化硅微球的浆液中, 通过低温加热处理基板让微球自动吸附其上, 氟化后的表面便具备了超疏水特性, 并且疏水效果随球体面积减小而增大。Ma 等人[39]通过静电纺丝法, 以四氢呋喃和二甲基甲酰胺溶液制备出直径范围在 150~400 纳米的纤维嵌段共聚物, 其水接触角为 163° 。Shiu [12]及其团队利用旋涂法将聚苯乙烯微球溶液涂抹于基板表面得到单分散的涂层。Huang 及其团队[40]通过化学气相沉积法控制碳纳米管阵列的生长, 制备出具有双层粗糙度的表面(如图 3 所示)。Zhao 等人[41]通过化学气相沉积法在硅衬底上由铁和铝作为催化剂合成垂直排列的多壁碳纳米管(CNTs)阵列, 氟化修饰后得到超疏水表面。Bormashenko 等人[42]采用蒸镀法, 将聚苯乙烯(PS)、聚碳酸酯(PC)和聚甲基丙烯酸甲酯(PMMA)等聚合物溶解在二氯甲烷(CH_2Cl_2)、氯仿(CHCl_3)等氯化溶剂, 通过结构间的自组装获得粗糙结构, 从而制备超疏水表面。

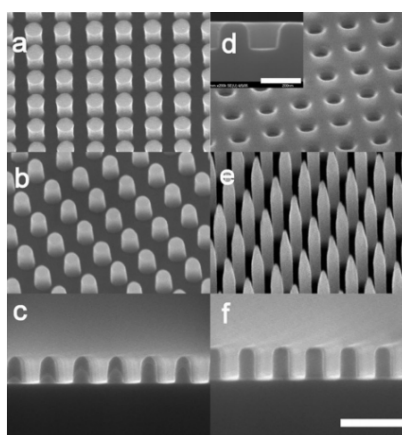


Figure 1. SEM images of (a-c) structure before hydrophobization; (d-f) structure after hydrophobization [17]

图 1. 表面结构的 SEM 图像: (a-c) 疏水化前的表面结构; (d-f) 疏水化后的表面结构[17]

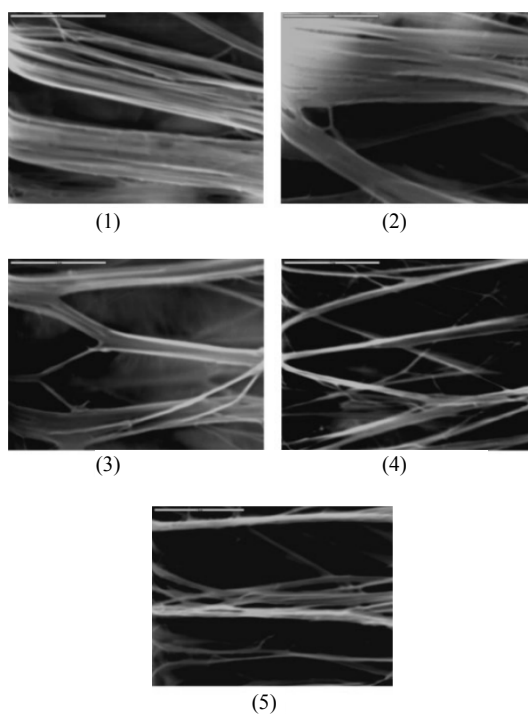


Figure 2. SEM images of the Teflon tape at different extension ratios: (1) $\epsilon = 5 \pm 5\%$; (2) $\epsilon = 35 \pm 5\%$; (3) $\epsilon = 90 \pm 5\%$; (4) $\epsilon = 140 \pm 5\%$; (5) $\epsilon = 190 \pm 5\%$ [36]

图 2. Teflon 胶带在不同延伸比下的 SEM 图像。(1) $\epsilon = 5 \pm 5\%$; (2) $\epsilon = 35 \pm 5\%$; (3) $\epsilon = 90 \pm 5\%$; (4) $\epsilon = 140 \pm 5\%$; (5) $\epsilon = 190 \pm 5\%$ [36]

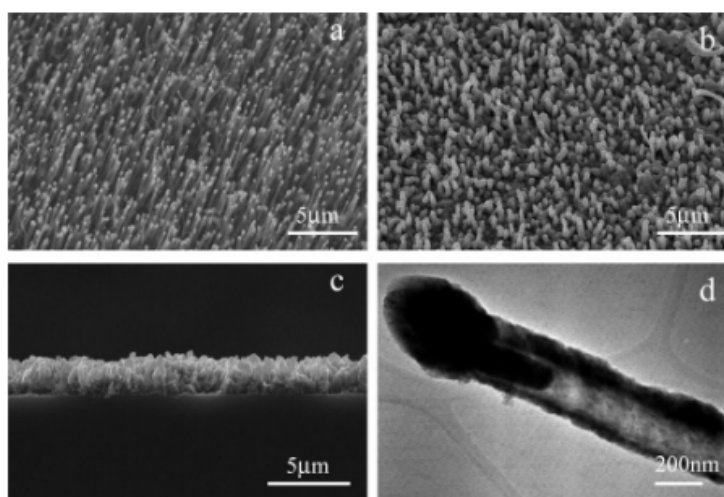


Figure 3. SEM images of (a) as-grown aligned CNT template, (b) topography of ZnO-coated CNTs, (c) cross-sectional view of ZnO-coated CNTs, and (d) TEM image of an individual ZnO-coated CNT [40]

图 3. SEM 图, (a) CNT 模板, (b) ZnO 涂覆的 CNT 的形貌, (c) ZnO 涂覆的 CNT 的截面图, 以及 (d) ZnO 涂覆 CNT 的 TEM 图像 [40]

5. 铸造法制备粗糙结构

Yabu 和 Shimomura 等人[43]在潮湿环境下利用含氟嵌段聚合物溶液, 制备出了多孔超疏水性透明薄

膜。透明性的实现是因为蜂窝状图案化薄膜的孔径在亚波长范围。Sun 及其团队[44]报道了一种纳米模板法构造超疏水 PDMS 表面的方法。他们首先使用荷叶作为原始模板制作了一个阴面 PDMS 模板, 然后使用阴面模板倒膜获得含有荷叶结构的 PDMS 模板。Zhao 及其团队[45]基于气相诱导相分离和 PDMS 表面富集的方法, 在潮湿环境中浇铸共聚物, 形成超疏水表面(如图 4 所示)。Lee 及其团队[46]利用纳米多孔氧化铝作为复制模板, 在温度及压力的驱动下, 采用纳米压印技术, 获得垂直排列的聚苯乙烯纳米纤维。随着聚苯乙烯纳米纤维长径比的增加, 纳米纤维不再垂直生长, 而是弯曲向下, 互相扭曲形成三维粗糙结构, 静态水接触角大约为 155° 。

6. 超疏水表面的应用

超疏水表面最基本的应用即来源于其自清洁能力, 水滴滚落或滑落的同时带走表面附着的污染物。在液体流动过程中, 为了达到自清洁的功能及较低的阻力, 除了接触角大之外, 超疏水表面还应该具有非常低的水接触角滞后(CAH)。前进角(contact advancing angle)和后退角(contact receding angle)是两个静态值, 它们之间的差值便被称为接触角滞后[47]。它是由于表面粗糙度和表面不均匀性而产生的。接触角滞后反映出了润湿/去湿循环的不可逆性, 它是液滴沿固体表面流动时能量耗散的一种量度。具有低接触角滞后的表面具有低的水倾斜角度, 它表示水滴滚落时表面必须倾斜的最小角度。水倾斜角越小, 越有利于颗粒污染物的去除。通常情况下, 我们将接触角滞后小于 10° 的表面称为自清洁表面。自清洁表面在各种应用中都广泛出现, 包括自清洁窗户、挡风玻璃、建筑、船舶、外墙涂料用具、屋顶瓦片、纺织品(如图 5 所示)、太阳能电池板等。并且, 在某些需要减小流体阻力的领域, 如排水管、微/纳通道等处也有超疏水的应用机会[48]。

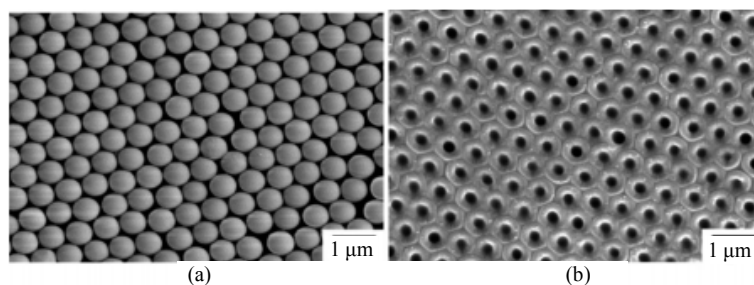


Figure 4. SEM images of (a) a two-dimensional PS microsphere array, (b) a PDMS negative replica [45]

图 4. SEM 图像, (a) 二维 PS 微球阵列, (b) PDMS 阴面模板[45]

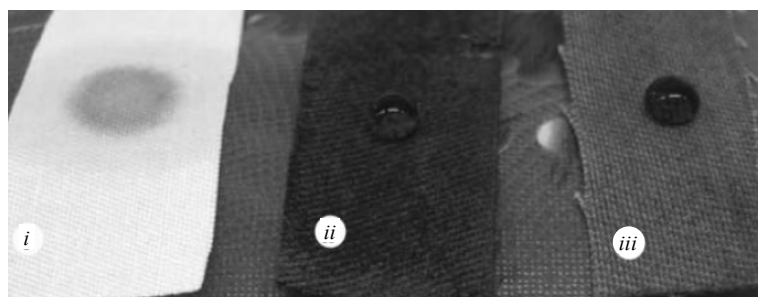


Figure 5. Water droplets on (i) untreated woven cotton sheet, (ii) CNT treated woven cotton sheet and (iii) poly (butyl acrylate)-CNT-treated woven cotton sheet [48]

图 5. 液滴在(i) 未处理的棉片, (ii) CNT 处理后的棉片, (iii) 聚丙烯酸丁酯-CNT 处理后的棉片[48]

另外,超疏水表面的最新进展使得其被用于节约能源[49]与能源转换[50][51]成为可能。首先,一个表面的疏水/亲水性能会显著影响毛细粘附力,反过来,也会影响固体表面滑动接触过程中摩擦和能量的耗散。选择合适的超疏水表面就可以降低能量的耗散。第二,超疏水和疏油表面,可以降低燃油运输过程中的损耗。第三,最近发现的可逆超疏水表面为新的能量转换提供了潜在可能,如微型毛细管发动机[51]。

湿润可能导致在静态或滑动接触过程中亲水性的固体之间的界面形成的凹形半月板[52]。这些半月板会产生负的压力进而导致一种内部吸引力,从而增加粘附力和摩擦力。在某些情况下,湿摩擦力可大于干摩擦力,而这通常是不利的[53]。另一方面,某些应用中,高黏附力则是有好处的,例如磁带和细胞生物材料表面的粘附。因此,增强润湿性在这些应用中是有利的[54]。在磁存储设备和微/纳机电系统(MEMS/NEMS)中,需要极小的黏附力甚至没有粘附力和摩擦力。随着这些设备的尺寸减小,往往会由表面力来支配体积力,因此,如何减小粘附力和摩擦力成为了这些设备正常运行的一个挑战。以上原因使得非粘性超疏水表面的发展对许多新兴应用起到至关重要的作用[55][56]。

7. 总结及展望

受限于气-液层自身的不稳定性及微纳结构的脆弱性,超疏水材料的实用性大打折扣。在实际应用中,在海洋或输水管道等拥有高压、水流连续冲击或微生物附着的环境下,外界液体很容易渗透进微纳结构中破坏气-液层从而使表面丧失疏液效果。因此,开发出结构强度更高、拥有自修复能力的超疏水表面是接下来研究者的共同目标。例如,通过更合理的结构排列方式来提高材料的整体强度。另一方面,通过加热、紫外辐射等方式来实现聚合物超疏水表面的自修复[57]。另外,如何实现超疏水表面环保、经济的工业化生产也值得进一步研究。

基金项目

国家自然科学基金(No.11764003)。

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