

# 超疏水表面在血液接触类医疗器械中的应用进展

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**摘要:** 医疗器械与血液接触时易引发凝血、排斥等不良反应, 会显著增加感染风险。研究表明, 构建超疏水表面能够有效减少生物分子黏附, 改善溶血和凝血现象, 抑制微生物生长, 显著提升血液相容性, 因而在血液接触器械表面获得广泛应用。然而, 目前对超疏水表面与血液、细胞及细菌相互作用的机制仍缺乏系统性认知, 这在一定程度上限制了其进一步应用。为推进超疏水表面在医疗领域的应用与发展, 系统总结了当前超疏水表面的构建策略、方法及材料体系, 深入探讨了超疏水表面与血液中血浆蛋白、血小板和红细胞的相互作用机理。研究发现, 超疏水表面的特定微纳结构形貌能够有效调控表面与血液成分的暴露面积和可附着区域, 改变表面蛋白的吸附构型, 优化表面血液流动的流体动力学特性, 从而实现对表面血液相容性及其耐久性的精准调控。还全面综述了超疏水表面在植入式医疗器械、体外循环设备和伤口敷料等血液接触医疗器械中的创新应用, 证实超疏水涂层在该领域具有广阔的应用前景。最后, 前瞻性地指出了该领域面临的主要挑战, 包括涂层的长期稳定性、使用耐久性以及生物相容性综合评价体系的建立。研究结果为未来超疏水表面在医疗器械中的优化设计和临床转化提供了重要的理论支撑和实践指导, 对促进医疗器械表面改性技术的发展具有重要的参考价值。

**关键词:** 超疏水表面; 抗血栓栓; 血液相容性; 抗生物黏附; 表面抑菌

中图分类号: TB34 文献标志码: A 文章编号: 1001-3660(2025)10-0047-14

DOI: 10.16490/j.cnki.issn.1001-3660.2025.10.004

## Advance in Application of Superhydrophobic Blood-repellent Surfaces for Medical Devices

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**ABSTRACT:** When medical devices come into contact with blood, they typically trigger the body's coagulation mechanisms and rejection responses, leading to hemodynamic interactions between them and increasing the risk of bacterial infections on the device surface. This results in a series of adverse reactions during clinical use, such as coagulation effects, thrombosis formation, hemolysis, protein adhesion, and microbial infections. Recent studies find that constructing superhydrophobic surfaces on blood-contacting surfaces can reduce biomolecule adhesion, improve hemolysis and coagulation, enhance blood compatibility,

收稿日期: 2024-11-19; 修订日期: 2025-03-28

Received: 2024-11-19; Revised: 2025-03-28

基金项目: 国家自然科学基金项目 (22008151); 上海健康医学院高水平地方高校建设项目 (E1-2602-21-201006-1); 上海健康医学院科研骨干学术导师制项目 (E3-0200-21-201012-8)

Fund: National Natural Science Foundation of China (22008151); The Excellent Doctoral/Master Dissertation Training Program of Shanghai University of Medicine & Health Sciences (E1-2602-21-201006-1); Academic Mentorship for Scientific Research Cadre Project (E3-0200-21-201012-8)

引文格式: 程静, 李政浩, 李欣怡, 等. 超疏水表面在血液接触类医疗器械中的应用进展[J]. 表面技术, 2025, 54(10): 47-60.

CHENG Jing, LI Zhenghao, LI Xinyi, et al. Advance in Application of Superhydrophobic Blood-repellent Surfaces for Medical Devices[J]. Surface Technology, 2025, 54(10): 47-60.

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and inhibit surface microbial growth. This has become an effective strategy for improving the blood compatibility of medical device surfaces and is widely applied to blood-contacting medical devices. However, the mechanisms of interaction between superhydrophobic surfaces and blood, cells, and bacteria are not yet fully understood, which limits their further medical application. To promote the application and development of superhydrophobic surfaces in the medical field, this paper summarizes the current methods for constructing superhydrophobic surfaces, the materials used, and the mechanisms behind their blood compatibility.

There are two main methods for constructing superhydrophobic surfaces: single-step and multi-step. The single-step method completes both the micro/nano-structure construction and low surface energy modification in a single process, such as sol-gel, electro-spraying, deposition, 3D printing, chemical etching, laser ablation, photolithography, and template methods. The multi-step method first prepares the surface micro/nano-structure and then modifies it with low surface energy materials. The materials used for constructing superhydrophobic surfaces include metals, metal oxides, phosphides, carbon-based nanoparticles, fluorinated chemicals, organosilicon compounds, polymers, and biomolecules.

This paper discusses the interactions between superhydrophobic surfaces and plasma proteins, platelets, and red blood cells in blood. The excellent blood compatibility of superhydrophobic surfaces is attributed to the Cassie state. Specifically, the micro/nano-structure morphology of superhydrophobic surfaces significantly affects the interactions between blood cells and bacteria. For example, high-curvature nanostructures are less likely to be adhered to by plasma proteins. Modifying the spacing, distribution density, curvature, and aspect ratio of micro/nano-structures can adjust the adhesion of blood cells and bacteria on superhydrophobic surfaces.

This paper also summarizes the mechanisms of superhydrophobic surfaces in resisting blood adhesion, including the reduction of the effective attachment area for blood cells and unique fluid dynamic properties. For example, in platelet adhesion, superhydrophobic surfaces not only inhibit platelet adhesion by reducing the effective attachment area but also further reduce the chances of platelet contact with the surface through their unique fluid dynamics, thereby exhibiting excellent anti-platelet adhesion properties.

Additionally, the paper reviews the application of superhydrophobic surfaces in blood-contacting medical devices, specifically in the following categories: 1) implantable medical devices, such as heart or vascular implants, cardiac valves, occluders, vascular stents, and bone implants; 2) extracorporeal circulation devices, such as blood purification and dialysis devices, cardiopulmonary bypass equipment; and 3) wound healing applications, such as antibacterial and hemostatic dressings.

The application of superhydrophobic coatings on surfaces of blood-contacting medical devices has great potential, especially in reducing thrombosis and preventing infections. These coatings effectively prevent the adhesion of blood components and bacteria due to their high apparent contact angle, low surface energy, and complex surface structure. However, current challenges including the stability, durability, and comprehensive evaluation of the biological compatibility of the coatings, require further research and resolution.

Future research should focus on several areas: first, having in-depth understanding of the interaction between superhydrophobic surfaces and blood under dynamic flow conditions, to optimize their anti-fouling and anti-thrombosis performance. Second, exploring cost-effective and easy-to-manufacture methods for preparing superhydrophobic surfaces to enhance their feasibility and sustainability in practical applications. Furthermore, the long-term stability and biocompatibility of superhydrophobic materials need to be further evaluated to ensure their safety and effectiveness in long-term use across various clinical environments.

In summary, superhydrophobic coatings hold great promise as a potential solution for blood-contacting medical devices in the future. Despite the challenges, continuous progress in technology and research will provide broad prospects for their application and development.

**KEY WORDS:** superhydrophobic surface; anti-thrombosis; blood compatibility; anti-biofouling; surface antibacterial

血液接触型医疗器械在医疗领域中扮演着关键角色, 包括外部接入器械(如透析回路、心肺转流回路及模式氧合器等)留置型器械(如静脉插管和中心

静脉导管)以及植入型器械(如冠状动脉支架、心脏瓣膜及心脏封堵器)。这些器械的使用时间各不相同, 从几小时到数周至数月不等, 甚至可能长达数年或终

生。随着器械与人体接触深度和时间的增加,其潜在风险也相应增加<sup>[1]</sup>。当这些器械或材料与血液接触时,会引发一系列生理过程,包括血浆蛋白吸附、凝血级联反应、补体系统激活、细胞炎症反应以及血小板激活等,最终可能导致溶血和血栓形成,影响器械的性能<sup>[2-4]</sup>。据报道,全球心血管器械市场在 2023 年的规模为 613.9 亿美元。血栓形成与多达 80% 的心脏支架死亡案例有关<sup>[5-6]</sup>。此外,血液接触的器械在使用过程中,易形成表面蛋白质层,促进葡萄球菌、铜绿假单胞菌等微生物的附着,并形成生物膜<sup>[7-8]</sup>。与游离状态的细菌相比,镶嵌在生物膜中的细菌更容易导致炎症反应、增加感染风险,进而成为重大公共卫生问题,并造成严重的经济损失<sup>[9]</sup>。因此,改善血液接触器械的血液相容性和耐菌性是研发的关键步骤,也是当前的研究热点<sup>[10-11]</sup>。

目前,各种涂层已经被开发用于改善表面的血液相容性,主要策略包括通过构建钝化层减小表面与蛋白质的相互作用,如表面接枝聚乙二醇(PEG)、自组装单分子层、表面沉积白蛋白、水凝胶和聚合物刷子<sup>[12]</sup>。还可以通过积极干预凝血级联反应来实现,例如表面接枝抗凝血药物如肝素<sup>[13]</sup>,修饰可释放一氧化氮(NO)的涂层<sup>[14]</sup>以及在器械表面上接枝比伐利鲁定、布飞林、阿加曲班或蛭蛭素等药物,用于控制凝血反应<sup>[15-17]</sup>。虽然已经在一定程度上改善了血液相容性,但仍未能完全抑制表面诱导的凝血现象。一方面,表面防污涂层在少量凝血因子吸附后可能失效,从而激活自我放大的凝血机制,导致凝血级联反应和血栓形成。另一方面,生物功能涂层虽然具有特定的生物活性,但有可能会干扰患者的药物治疗,且往往无法防止污垢的积累,因此其表面很快被蛋白质覆盖,导致功能失效<sup>[18]</sup>。

受自然界生物体如荷叶、莲花、蜻蜓翅膀等润湿现象和形貌特征的启发,制备了具有超疏水性能的材料<sup>[19-20]</sup>。超疏水材料与水溶液静态接触角大于  $150^\circ$ ,滚动角小于  $10^\circ$ ,接触角(Contact Angle)是液体与固体表面接触时形成的角度,而滚动角(Rolling Angle)指的是液滴在表面上开始滚动时与水平面之间的角度。这些参数对于评估表面的疏水性至关重要。超疏水表面通常由微米或纳米级的粗糙结构与低表面能材料共同作用,因而具有抗污染、自清洁的特性,超疏水材料在液体减阻、化学屏蔽、抗冰性、微型机器人、防腐蚀涂层、增强滴状冷凝,以及液滴的受控操纵等领域有广泛的应用<sup>[21-29]</sup>。近年来,超疏水表面与水或者血液等生物液体接触时,可以有效减小细胞、蛋白和表面的接触面积,降低血液在表面的剪切率,从而具有较好的血液相容性、止血性能、抗组织粘连和抗菌性的效果<sup>[30]</sup>,预示了超疏水材料在改善器械的血液相容性方面有广泛的潜在应用<sup>[31]</sup>。然而,目前关于超疏水材料血液相容性机制的理解尚不明

确,限制了其在医疗领域的进一步应用<sup>[32]</sup>。为了解析超疏水材料与血液相容性之间的关系,2017 年,Jokinen 等<sup>[33]</sup>主要探讨了超疏水材料与血小板的相互作用机制,并综述了自 2017 年以来超疏水材料在血液相容性改善方面的应用。然而,关于超疏水材料与血液中其他成分的相互作用,特别是在实际临床应用中的表现,相关研究仍然较少。2019 年,裴阳阳等<sup>[34]</sup>深入探讨了仿生超疏水材料的抗菌性,集中讨论了细菌与仿生超疏水材料的相互作用,但关于超疏水材料与血液复杂成分相互作用的综述仍然较为缺乏。因此,超疏水材料的血液相容性机制仍需要进一步深入研究,以促进其在医学领域的广泛应用。基于此,本文首先梳理了现有超疏水材料的构建策略和合成方法以及构建超疏水材料的化学成分,并且对现有制备方法进行了总结和比较。随后,将重点讨论超疏水材料微纳结构和低表面能与血液中血红细胞、血小板及蛋白之间的相互作用原理,包括其在减小细胞、蛋白质接触面积、减小血液在表面的剪切率等方面所具备的生物学功能。最后,将列举近 5 年疏水材料在医疗器械表面的应用案例,为未来超疏水材料在改善血液器械表面生物相容性的研究和应用提供参考。

## 1 超疏水表面的构建和原理

### 1.1 超疏水材料的构建

超疏水表面通常具备微纳结构和低表面能的特性。目前,构建超疏水表面的主要策略有 3 种:即“直接成型”“自下而上”(Bottom-up Methods)和“自上而下”(Top-down Methods)<sup>[35]</sup>。如图 1 所示,直接成型的策略是将金属、无机非金属、纳米材料和有机材料直接制备超疏水材料,代表性的方法有静电纺丝、3D 打印<sup>[36]</sup>等,直接成型的方法可以实现超疏水物体的一体成型,具有高自由度和个性化定制的优势,尤其适用于复杂形状或小批量生产,但其速度较慢且材料种类有限。“自下而上”策略指的是用在表面增加涂层的方法构建出低表面能的微纳结构。代表性的制备方法包括喷涂法<sup>[37-39]</sup>、浸涂法<sup>[40-41]</sup>、沉积法<sup>[42-43]</sup>、溶胶凝胶法以及层层自组合法<sup>[44]</sup>等,具有简单、适合规模化生产的特点。而“自上而下”策略则是指通过刻蚀等去除材料的方法构建出低表面能的微纳结构,如模板图案<sup>[45]</sup>、微压模塑<sup>[46]</sup>和等离子体蚀刻<sup>[47]</sup>等技术,对仪器要求较高,且工艺较为复杂,适合高精度、耐久性较高的器件加工。其制备过程主要分为一步法和多步法,如图 1 所示。一步法即在单一过程或步骤中同时完成微纳结构的构建和低表面能物质的修饰。多步法则首先制备表面的微纳结构,然后在此基础上进行低表面能物质的修饰,如 Manivasagam 等<sup>[48]</sup>利用热硫酸化学刻蚀钛表面以形成微纳米结构,随后通过氟硅烷修饰降低表面能,使

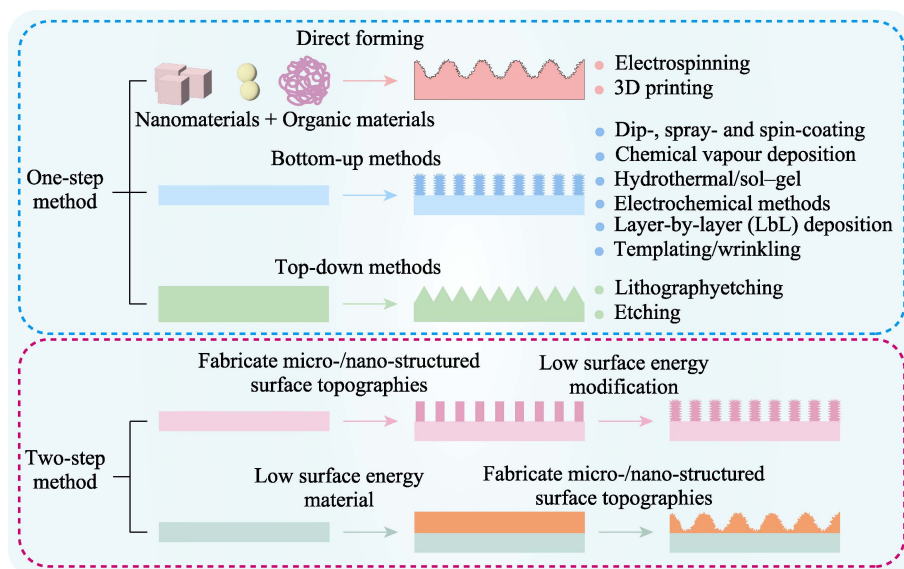


图1 超疏水材料的构建方法和策略示意图

Fig.1 Schematic diagram of methods and strategy for constructing superhydrophobic materials

其具备超疏水性能。

表面微纳结构的构建材料包括金属、金属氧化物、磷化物、碳族纳米颗粒、聚合物及生物大分子等,如表1所示。金属、金属氧化物、磷化物和碳族纳米颗粒等通常用于构建这些微纳结构,而含氟化学品和有机硅等有机化合物则用于降低表面能。Naderizadeh等<sup>[37]</sup>采用喷涂法在铝片表面喷涂氟化的 $\text{SiO}_2$ ,实现了超疏水表面的制备。Liu等<sup>[40]</sup>通过浸涂法,在普通棉纱布上依次沉积了壳聚糖(CS)、没食子酸修饰的银纳米颗粒( $\text{GA@AgNPs}$ ),以及1H,1H,2H,2H-全氟癸硫醇(PFDT),获得具有超疏水性能的纱布。Zeng等<sup>[42]</sup>运用电泳沉积技术在医用不锈钢表面制备了花状磷化钛( $\text{TiP}$ )、壳聚糖( $\text{CHI}$ )、全氟癸烷(PFOTS)复合涂层,该涂层不仅具有优异的超疏水性能,还表现出显著的抗血液黏附和抗菌性能。Seyfi等<sup>[41]</sup>利用浸涂法,在热塑性聚氨酯(TPU)基底表面涂覆了聚二甲基硅氧烷(PDMS)和不同含量的磷酸银( $\text{Ag}_3\text{PO}_4$ )纳米颗粒涂层,使超疏水涂层具备良好的抗菌和低蛋白吸附性能。Lai等<sup>[46]</sup>通过碳化硅( $\text{SiC}$ )涂覆的筛网模板,借助微压模塑技术在聚丙烯(PP)表面构建超疏水涂层,该涂层表现出优异的耐久性和抗菌性,见图2。Kang等<sup>[49]</sup>在Mg-Gd-Nd-Zn-Zr合金基底上使用一步水热法沉积了超疏水羟基磷灰石涂层,展示了其在医用材料中的应用潜力。Zhou等<sup>[50]</sup>采用激光刻蚀和硬脂酸修饰法,成功制备了超疏水双极电凝夹,该夹具有出色的抗黏附性、优异的导电性和良好的耐久性,为电外科手术领域带来了新的应用前景。

## 1.2 固体表面浸润理论

材料表面的浸润性反映了液体在材料表面的润

湿特性,可以通过水滴在材料表面形成的接触角(Contact Angle, CA)来表征,并先后发展出了几种理论模型。如图3a所示,假设理想固体表面是光滑平整、化学均匀、不可溶和惰性的,固、液、气界面可达到自由能的热力学平衡,静态接触角 $\theta_Y$ 可以根据杨氏方程进行计算<sup>[68]</sup>:

$$\cos \theta_Y = \frac{(\gamma_{SV} - \gamma_{SL})}{\gamma_{LV}} \quad (1)$$

式中: $\theta_Y$ 为材料的本征接触角; $\gamma_{SV}$ 、 $\gamma_{SL}$ 和 $\gamma_{LV}$ 分别为固体/气体、固体/液体和液体/气体界面张力。通常,当表面与水的接触角 $\theta_Y > 90^\circ$ 时,认为该表面是疏水的,而当 $\theta_Y < 90^\circ$ 时,认为该表面是亲水的。杨氏方程的局限在于它仅适用于理想的光滑固体表面。

实际材料表面存在一定的粗糙度,因此针对材料粗糙表面,Wenzel和Cassie等的理论模型对杨氏方程进行了修正。如图3b所示,Wenzel<sup>[69]</sup>模型理论假设了液体与粗糙材料表面接触时,液滴总是占据填充在粗糙的微纳结构中,引入表面粗糙度因子 $r$ 以表示实际面积和投影面积之比,并提出了表观接触角 $\theta_w$ 与本征接触角 $\theta_Y$ 的关系:

$$\cos \theta_w = r \frac{(\gamma_{SV} - \gamma_{SL})}{\gamma_{LV}} = r \cos \theta_Y \quad (2)$$

式中: $\theta_w$ 表示粗糙材料表面的表观接触角; $\theta_Y$ 表示材料的本征接触角。因此, $r$ 可作为Wenzel状态下疏水性或亲水性的放大因素,但当材料表面非常粗糙或多孔时,理论模型受到限制。如图3c所示,Cassie模型被进一步发展和提出,认为当材料表面接触液滴时,液滴不会完全填满或浸润微纳粗糙结构,而是悬浮于粗糙表面之上,捕捉的空气层被包裹在液体和材料表面之间。因此,基于Wenzel模型,Cassie等<sup>[70]</sup>



表 1 构建超疏水表面所用的材料和方法  
Tab.1 Materials and methods for constructing superhydrophobic surfaces

Micro/Nano Structure		Low Surface Energy Materials	Methods	References
Metals & Metal Oxides	Ag nanoparticles	1H,1H,2H,2H-Perfluorodecanethiol (PFDT)	Dip-coating	[40]
	ZnO nanoparticles	PDMS, stearic acid (STA)	Spray-coating, Dip-coating	[38,51]
	TiO <sub>2</sub> nanoparticles	PDMS	—	[52]
	MnO <sub>2</sub> nanoparticles	STA	In-situ impregnation	[53]
Metal Phosphides	TiP	Perfluorooctyltrichlorosilane (PFOTS)	Electrophoretic deposition	[42]
Phosphates	Ag <sub>3</sub> PO <sub>4</sub>	PDMS	Dip-coating	[41]
	Hydroxyapatite	—	Hydrothermal method	[49]
Carbon-Based Nanoparticles	Fluorinated graphene (GO), MWCNTs	Polyurethane (PU)	Dip-coating	[54]
	Carbon nanofibers (CNFs)	PTFE or PDMS	Dip-coating	[55]
	Carbon black	PDMS	Dip-coating	[46,56]
Silicon-Based Nanoparticles	SiC	PP	Template method	[39]
	SiO <sub>2</sub>	PFDTMS, octyltriethoxysilane (OTS), PDMS	Chemical deposition, electrodeposition, hydrothermal, spray-coating	[39, 43, 57]
	—	PDMS	Mild flame treatment	[58]
	Si	—	Plasma treatment, chemical etching	[59]
	Aluminosilicate	Octylamine	Evaporation-induced self-assembly	[44]
Polymers	Nitrile rubber (NBR)	Vinyltriethoxysilane (VTES)	Dip-coating	[60]
	PTFE/PVDF	—	Plasma treatment	[47]
	Synthetic polymers Polypropylene hollow fiber membrane (PPHFM)	Glycidyl methacrylate (GMA), perfluorooctanoyl chloride	Dip-coating	[61]
	Polystyrene (PS)		Electrospinning	[36]
	Natural polymers Tannic acid (TA), cellulose nanocrystals (CNCs)	Octadecylamine (ODA)	Spray-coating	[62]
Metal-Organic Frameworks (MOFs)	ZIF-8	Silane coupling agent	Spray-coating	[63-64]
	Cu-MOFs, Zn-MOFs	STA	Dip-coating	[65]
Protein Molecules	Porous polypyrrole-amine	Bovine serum albumin (BSA)	Grafting	[66]
Biomolecules	Denatured lysozyme	Carnauba wax	Spray-coating	[67]

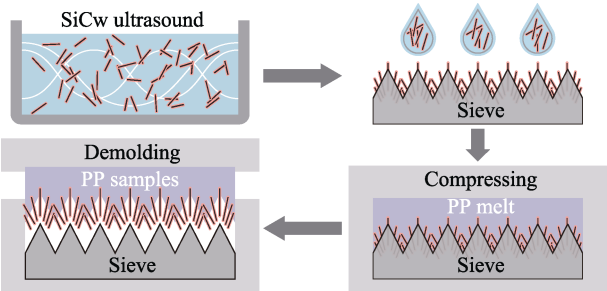


图 2 SiCw 浸渍筛网模板, 微压模塑在聚丙烯 (PP) 表面构架超疏水过程<sup>[46]</sup>

Fig.2 SiCw-impregnated mesh template, micro-pressure molding for superhydrophobic construction on polypropylene (PP) surface<sup>[46]</sup>

提出了复合表面接触的 Cassie-Baxter 方程:

$$\cos \theta^* = f_1 \cos \theta_1 + f_2 \cos \theta_2 \tag{3}$$

式中:  $\theta^*$  为复合表面的表观接触角;  $\theta_1$  代表液滴与材料相的本征接触角;  $\theta_2$  代表液滴与气体相的本征接触角;  $f_1$  和  $f_2$  分别代表固-液、液-气界面的接触面积占比 (  $f_1 + f_2 = 1$  )。

在 Cassie 状态下, 假设空气完全排斥液体, 液体悬浮于微纳结构之上,  $\theta_2$  为 180°时, Cassie 方程可以改写为:

$$\cos \theta^* = f_1 \cos \theta_1 - f_2 = f_1 (\cos \theta_1 + 1) - 1 \tag{4}$$

Wenzel 和 Cassie 作为 2 种经典理论模型可在很

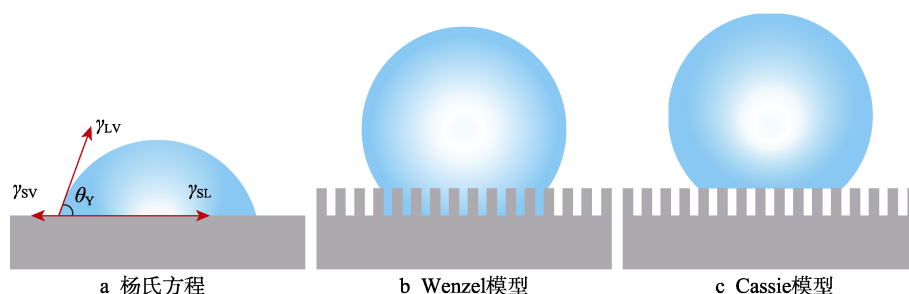


图 3 固体表面的浸润理论

Fig.3 Wetting theory of solid surfaces: a) Young's equation; b) Wenzel model; c) Cassie model

大程度上分别解释超亲水表面和超疏水表面的浸润现象。然而 Wenzel 和 Cassie 模型仅在特定条件下适用于超疏水表面,对于表面复杂结构如纳米级多孔结构或层次化纳米/微米结构的情况,或者动态润湿行为则不适用<sup>[71]</sup>。由于液体在不同表面上的运动情况复杂,所以亟待进行新的模型探索。

## 2 超疏水材料的生物学功能

### 2.1 超疏水表面血液相容性

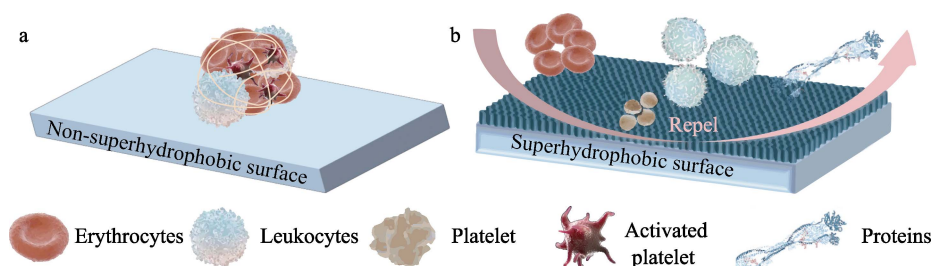
血液是一种复杂的生物液体,包含血小板、红细胞、蛋白质、凝血因子、代谢物等多种化学成分,具有不同的尺寸,其中蛋白如纤维蛋白原的尺寸为 10~50 nm,血小板的尺寸为 2~3 μm,红细胞的尺寸为 6~8 μm,白细胞的尺寸为 12~15 μm<sup>[72]</sup>。当医疗器械及其材料与血液接触时,蛋白质会吸附到表面形成促凝和促炎的活性界面,从而引起外源性或者内源性的凝血反应,可能存在的反应有:血液中哈格曼因子(因子 XII)的接触激活,启动一系列酶促反应,最终导致凝血因子 XI 和 IX 的激活,产生关键的凝血酶;凝血酶激活血小板并形成纤维蛋白;同时,血小板在器械表面的附着和激活也可能发生;在血栓形成过程的最后阶段,聚集的血小板和聚合的纤维蛋白形成稳定的血块<sup>[3]</sup>。

总之,可以将凝血反应过程分为血浆蛋白质的表面吸附、血小板的黏附与激活、补体系统的激活以及纤维蛋白的交联等 4 个反应路径<sup>[2,12]</sup>。通过抑制或中断其中任何一个路径,可以显著改善血液相容性,从而发挥抗凝血和抗血栓的作用。超疏水表面因其特殊

的微纳结构和较低的表面自由能,能有效减少血小板、血细胞及其他成分的相互作用和吸附,从而抑制和减缓血液凝结过程,如图 4 所示。具体来说,超疏水表面与血液成分的相互作用不同,而表现出优异的血液相容性。

#### 2.1.1 超疏水表面与血浆蛋白相互作用

将血液接触器械表面的蛋白质吸附是血栓形成途径中的第一个现象,可能源自损伤部位的细胞,可以介导血小板沉积和血栓形成<sup>[15]</sup>。吸附在表面的蛋白质形成一个复合物,包括胶原蛋白、高分子量激肽原、前卡利克雷因和因子 XII,吸附的蛋白质可以诱导血小板附着,因此,防止蛋白质沉积和吸附器械表面是提高其血液相容性的第一步<sup>[17]</sup>。血浆蛋白中的白蛋白和纤维蛋白原是研究血液与表界面作用中代表性的 2 种蛋白质。白蛋白吸附在表面可以防止其他蛋白质附着,间接减少血小板活化和黏附。纤维蛋白原附着到表面能与血小板整合素受体特异性结合,导致血小板激活<sup>[30,72-73]</sup>。超疏水的微纳结构对血浆蛋白的黏附量和构象都有显著的影响。如超疏水表面血液处于 Cassie-Baxter 状态下,超疏水表面接触液体时形成气体层,减小了液体与固体接触面积,显著减少了血浆蛋白和血细胞的黏附。而液滴在 Wenzel 状态时,即表面被浸润,血浆蛋白的吸附量显著增加。此外,超疏水表面的曲率会影响吸附血浆蛋白的构象<sup>[73]</sup>,如纤维蛋白原在高曲率的表面上被拉伸或变形,继而影响了与血小板的相互作用和抑制凝血<sup>[33]</sup>,如图 5d 所示。而具有球形结构的小分子蛋白(如白蛋白)能在高曲率表面不易发生变形。高曲率超疏水表面可以有效减少蛋白质的吸附,并抑制蛋白质的二聚化和聚集<sup>[72]</sup>。

图 4 非超疏水 a) 和超疏水表面 b) 与血液的相互作用<sup>[32]</sup>Fig.4 Interaction between non-superhydrophobic a) and superhydrophobic b) surfaces with blood<sup>[32]</sup>

再者, 超疏水表面的微纳结构还会影响液体在表面的流动行为, 进而影响蛋白质的吸附。例如, 在高剪切流场下, 蛋白质的吸附量可能会减少, 因为蛋白质可能在流动过程中被冲走, 尤其是在表面为 Cassie 状态时。总之, 超疏水的表面形貌对不同血浆蛋白的黏附量和黏附状态都有不同的影响。

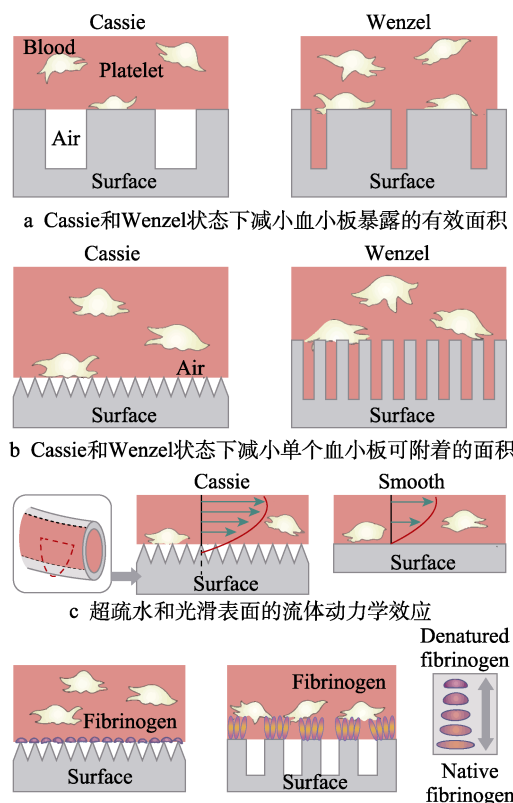
### 2.1.2 超疏水表面与血小板相互作用

超疏水表面在抑制血小板黏附和活化方面表现出良好的效果。例如, Li 等<sup>[67]</sup>通过半胱氨酸诱导溶菌酶 (PTL) 相变聚集成纳米颗粒, 并在纤维素基材料表面形成具有微观/纳米拓扑结构的致密层。经过卡那巴蜡疏水修饰后, 超疏水涂层能抵抗血液和生物流体浸润, 显著减少血小板附着。另外, Sun 等<sup>[74]</sup>制备了一种氟代烷基侧链掺杂的聚碳酸酯脲 (FPCUs) 修饰的定向碳纳米管 (ACNT) 超疏水薄膜, 该薄膜能显著减少血小板附着, 并保持血小板未激活状态。Ozkan 等<sup>[75]</sup>将十七氟癸基三乙氧基硅烷 (FAS-17) 修饰的 ZnO 和 Cu 纳米颗粒涂覆在海绵表面, 并通过 PDMS 固化, 成功制备了具有超疏水性能的海绵。实验结果表明, 该涂层能够显著减少 64% 的血小板黏附和活化。此外, Zhang 等<sup>[76]</sup>采用紫外激光照射和超声酸刻蚀方法, 在 Ti 金属表面制备了微纳结构, 并通过全氟烷基硅烷 (PTES) 进行修饰, 成功获得了超疏水表面。体内实验显示, 这种表面具有优异的抗血小板和血细胞黏附能力。最后, Celik 等<sup>[77]</sup>首次将打印纸的纹理复制到 PDMS 柔性膜表面, 并通过巴西棕榈蜡胶体沉积与打磨处理, 制备了不含纳米颗粒的超疏水柔性膜。该膜对全血及其组分 (如血小板悬液、红细胞浓缩物和新鲜血浆) 表现出卓越的抗吸附能力和抗凝效果, 能够延迟凝血时间至少 1 h。

超疏水表面抗血小板黏附的机制主要归因于有效附着 4 个解释机理, 如图 5 所示。如图 5a 所示, 减小血小板暴露的有效面积, 在 Cassie 状态下, 超疏水表面的微纳结构使血小板只能与表面微小高峰发生相互作用, 从而减小了整体有效表面积, 进而减少了血小板的附着。而在 wenzel 状态下, 血小板有可能附着在微纳结构的底端, 这也与微纳结构的尺寸有关, 若微纳结构的间距大于  $2\ \mu\text{m}$ , 血小板溶液被黏附在被浸润的微纳结构底端。如微纳结构小于  $2\ \mu\text{m}$  时, 即使在 Wenzel 状态下, 血小板也不能黏附在微纳结构的底端。如图 5b 所示, 减小单个血小板可附着的面积, 在 Cassie 和 Wenzel 状态下曲率越高, 血小板的黏附面积越小, 因此表面的吸附量显著减少。如图 5c 所示, 产生流体动力学效应, 从而减少血小板的附着。如图 5d 所示, 改变血液中蛋白的吸附量和构象, 从而减少血小板的附着<sup>[30]</sup>。Chen 等<sup>[78]</sup>提出了一种基于血小板 ( $2\ \mu\text{m}$ ) 和血小板伪足 ( $50\ \text{nm}$ ) 大小的划分方法。根据这一划分, 微观结构的特征尺度大于  $2\ \mu\text{m}$  时, 尺度越大, 血小板附着力越强; 微观

结构的特征尺度小于  $50\ \text{nm}$  时, 则会导致血小板附着力越小; 当微观尺寸在  $50\ \text{nm}\sim 2\ \mu\text{m}$  时, 表面微观结构的顶部面积越小, 即结构越尖锐, 有助于减少血小板的吸附<sup>[79]</sup>。此外, 超疏水的微纳结构对血小板的活化也有显著影响, Movafaghi 等<sup>[80]</sup>发现氟化的纳米花表面相比氟化的纳米管表面显示出显著更高的血小板附着与激活, 这归因于超疏水材料的稳健性的保持。超疏水表面微观和纳米结构可以显著改变流体动力学流动模式, 大大减小表面的剪切力, 并抑制血栓形成。Yu 等<sup>[81]</sup>比较了立方体、四棱锥体和半球形 3 种不同超疏水表面形态对血液流动的影响。其中具有立方体凸起纳米结构超疏水表面的流体速度最高, 而半球形凸起超疏水表面有最多的涡流, 能够更好地抑制血栓的形成。

总之, 超疏水表面不仅通过减小有效附着面积来抑制血小板黏附, 还通过其独特的流体动力学特性, 进一步减少了血小板与表面接触的机会, 从而表现出优异的抗血小板黏附性能。



d 纤维蛋白在高曲率表面发生构象改变从而阻止血小板的黏附

图 5 超疏水表面抗血小板黏附的机理图<sup>[33]</sup>

Fig.5 Mechanism diagram of superhydrophobic surfaces against platelet adhesion<sup>[33]</sup>: a) reduction of effective area of platelet exposure in Cassie and Wenzel states; b) reduction of area available for individual platelet adhesion in Cassie and Wenzel states; c) hydrodynamic effects of superhydrophobic and smooth surfaces; d) conformational changes of fibrinogen on high-curvature surfaces, preventing platelet adhesion

### 2.1.3 超疏水表面与红细胞相互作用

在透析器、人工肺 (ECMO) 等体外循环医疗器

械使用过程中,血液在血泵和管路中的流动容易受到剪切应力,导致溶血现象的发生,从而限制了体外循环的使用时长<sup>[82]</sup>。超疏水表面能够有效减轻血液在泵送过程中对红细胞的损伤,其原因是超疏水材料表面为 Cassie 状态时,红细胞与材料的可黏附面积非常小,从而减小了红细胞与材料的相互作用。其次,超疏水表面特殊的流体动力学特点降低了表面的剪切力,使红细胞所受外力减少,进而减小了溶血的可能性。Li 等<sup>[83]</sup>研究发现超疏水表面可以降低血泵在各种工作条件下的溶血指数,其中血泵溶血指数的最大降低率为 22.9%。Wang 等<sup>[84]</sup>通过简单的热压成型方法,从阳极氧化铝模板中复制了以聚碳酸酯为主体材料的超疏水的仿生纳米柱表面。超疏水纳米柱状表面表现出优异的血液相容性,其溶血率远低于 5%。

2.2 超疏水表面的抗菌性能

医疗器械在使用过程中,与体液(例如血液和唾液)和寄生病原体滴液接触,容易被微生物黏附和污染。常见的细菌包括表皮葡萄球菌和金黄色葡萄球菌等革兰氏阳性细菌,以及铜绿假单胞菌、肠球菌等革兰氏阴性细菌(表 2)<sup>[8]</sup>。

细菌在医疗器械表面附着的主要过程包括细菌迁移到表面、细菌与界面相互作用以及细菌的增殖,最终在表面形成细菌生物膜<sup>[85]</sup>。超疏水涂层具有良好的抗菌性,并且可以有效抑制生物膜的形成和耐药菌的产生。Li 等<sup>[57]</sup>通过简单喷涂技术在 PU 表面制备出超疏水涂层,相比于 PU 有超疏水涂层的表面金黄色葡萄球菌计数从 120 cfu/cm<sup>2</sup>降低至 5.0 cfu/cm<sup>2</sup>。超疏水表面的纳米结构与其抗菌能力息息相关。Sadler 等<sup>[86]</sup>主要研究了表面的拓扑结构,特别是纳米柱的间距对 PDMS 涂层柱抗菌性能的影响,研究发现在相似的超疏水条件下(接触角均大于 150°),柱间距为 87.5 μm 时,金黄色葡萄球菌、大肠杆菌或口腔链球菌抑菌效率较高,3 种菌的附着量减少率均超过 99.9%。Zhao 等<sup>[87]</sup>通过有限元模拟了大肠杆菌细胞与纳米结构阵列之间的相互作用,并分析了纳米结构几何形状对细胞破裂速度的影响,研究发现除了减小纳米柱直径或纳米片的厚度/宽度、适当增加纳米结构间距外,通过增加纳米柱之间的高度差,也可以加速细胞破裂。当相邻纳米结构的高度差(ΔH)小于 40 nm 时,细胞破裂速度随着 ΔH 的增加而迅速增加;而当 ΔH 大于等于 40 nm 时,细胞破裂速度达到最大值并保持稳定。

表 2 医疗设备相关感染的微生物类型<sup>[8]</sup>  
Tab.2 Types of microorganisms associated with medical device-related infections<sup>[8]</sup>

Type of medical device-associated bacterial infections	Susceptible bacteria	
	Gram-positive bacteria	Gram-negative bacteria
Catheter-Related Bloodstream Infection (CRBSI)	<i>Staphylococcus epidermidis</i> , <i>Staphylococcus aureus</i> , <i>Enterococcus spp.</i>	<i>Pseudomonas aeruginosa</i> , <i>Klebsiella pneumoniae</i> , <i>Enterococcus spp.</i>
Prosthetic heart valve infection	<i>Staphylococcus epidermidis</i> , <i>Staphylococcus aureus</i> , <i>Streptococcus spp.</i>	—
Other Catheter-Related Bloodstream Infections	<i>Staphylococcus epidermidis</i> , <i>Staphylococcus aureus</i> , Coagulase-negative <i>Staphylococci</i> , <i>Streptococcus spp.</i>	<i>Pseudomonas aeruginosa</i> , <i>Enterococcus spp.</i>

以上研究表明,通过改变表面纳米结构的柱间距、分布密度、高宽比可以提升涂层的抗菌效果。除此之外,超疏水涂层的微纳结构也可以通过表面修饰改善抗污性和生物相容性,如 Yi 等<sup>[88]</sup>在 ZnO 纳米柱表面聚合两性离子聚合物 PSBMA,以铜绿假单胞菌(*P. aeruginosa*)为模型细菌,ZnO-PSBMA 表面在干燥状态下表现出超过 98%的高杀菌效率,并在湿润条件下可以释放约 99%的附着细菌,具有高效的再生能力。

3 超疏水材料在医疗器械领域的应用

基于超疏水材料与血液等生物液体接触时表现出的生物学性能,超疏水材料在实际医疗器械表面也有广泛应用。目前,超疏水材料在血液接触医疗器械方面的应用主要包括以下几类:1)植入类医疗器械,在心或血管内植入器械,如心脏瓣膜,封堵器,血管

支架等,以及骨植入器械等;2)体外循环器械,如血液净化和透析装置,心肺流转器械;3)抗菌止血的敷料,见图 6。

3.1 植入医疗器械

血液接触类植入医疗器械(如心脏瓣膜、封堵器和血管支架)在植入人体后常引发血栓、溶血等血液相容性问题。研究表明,通过在其表面构建超疏水涂层可显著提升器械的血液相容性。Zhang 等<sup>[76]</sup>利用紫外激光工艺、超声酸处理和化学改性,在医用纯钛基底上制造了可控的超疏水表面,处理后的钛合金具有高接触角、低水和血液附着性,将这种内表面超疏水的钛合金中空管植入兔子的左颈动脉,结果显示超疏水表面有效减少了血细胞的黏附和血栓形成,并未引起明显的炎症或过度增生。Pecha 等<sup>[89]</sup>对血管移植植物表面进行了二氧化硅(SiO<sub>2</sub>)纳米颗粒的修饰,赋予其超疏水特性。这种超疏水涂层极大地抑制了细菌的



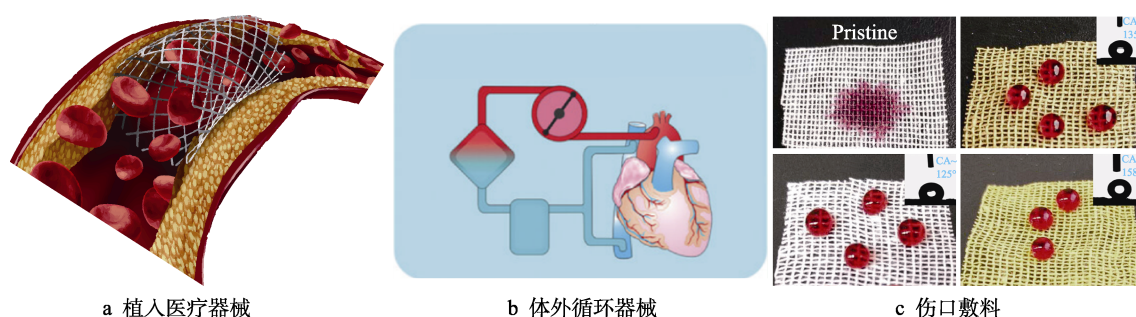


图 6 超疏水材料在医疗器械领域的应用

Fig.6 Applications of superhydrophobic materials in medical devices a) implantable medical devices, b) extracorporeal circulation, c) wound dressings

生长, 在人工灌流实验中未对血细胞产生负面影响。

Ling 等<sup>[90]</sup>利用溶剂热法, 在羟基磷灰石 (HA) 改性的镁合金表面合成了铜 ( $\text{Cu}^{2+}$ ) 掺杂的沸石咪唑醇框架-8 (ZIF-8) 涂层。随后, 通过十二烷硫醇 (DDM) 和肉豆蔻酸 (MA) 混合乙醇溶液的疏水处理, 获得了超疏水性能。这种超疏水涂层在可见光辐照后生成光电子, 从而产生能够清除还原型十二烷硫醇的活性氧化物, 使表面从超疏水转变为亲水性。这种浸润性转变满足了植入物在不同临床阶段的表面功能需求。改性的镁合金复合涂层在超疏水到亲水的转变后, 促进了成骨细胞的附着和生长。

另外, Mg 合金表面制备了一个基于两阶段纳米片状结构的羟基铁复合涂层, 经过热还原处理以去除表面的 OH 键, 并呈现超疏水性, 这有助于在植入体进入人体之前维持其清洁和抗腐蚀性能。Mg 合金表面的超疏水性能可通过浸泡 75% (体积分数) 乙醇溶液去除, 以进一步适应生物应用。此外, 涂层颜色从黄色变为棕黑色, 增加了光吸收, 产生优异的光热效应。涂层中  $\text{Fe}^{2+}$  含量增加的缺陷还显著提高了过氧化物酶的活性, 从而对细菌和肿瘤表现出协同的光热/化学动力学治疗效果<sup>[91]</sup>。

### 3.2 体外循环器械

体外循环器械及其相关部件, 如体外膜氧合器 (ECMO)、心脏辅助装置 (VAD) 和心肺转流器, 广泛用于维持血液体外循环和氧合功能。虽然这些器械在临床上有重要应用, 但由于剪切诱导的血细胞损伤和器械本身引发的血栓形成, 常导致不良事件和潜在致命的并发症, 如设备故障、缺血性/栓塞性中风、溶血性贫血以及急性肾损伤<sup>[92]</sup>。传统上, 通过给予肝素、一氧化氮、白蛋白、聚-2-甲氧基乙基丙烯酸酯和磷酸等抗凝剂来解决血栓形成问题, 但这些方法未能解决由过度剪切应力引起的血液损伤问题<sup>[93]</sup>。

超疏水表面被广泛应用于体外循环器械及其管道, 以改善其血液相容性。例如, Sun 等<sup>[30]</sup>制备了一种高血液相容性且无生物毒性的超疏水抗血液附着管道。超疏水处理显著延长了管道的凝结时间, 同时减少了管道表面的蛋白质和血小板吸附, 分别减少了

32%和 74%。另外, Li 等<sup>[83]</sup>报道了具有超疏水表面的血泵相较于传统血泵, 水力效率显著提升, 最大增幅达 13.9%。Yi 等<sup>[94]</sup>在多孔氟聚合物 (PVDF-HFP) 氧合基膜表面开发了超疏水结构, 通过电喷雾在多孔膜表面沉积 PVDF-HFP 纳米颗粒, 并用全氟硅烷修饰, 获得了超过  $150^\circ$  的接触角。这种表面不仅具有出色的抗污染性能, 还保持了良好的血氧合性能。Tan 等<sup>[95]</sup>将强效抗血栓化合物嫁接到超疏水聚四氟乙烯泡沫表面微结构的尖端, 以同时实现减阻和抗血栓作用, 使材料能够用于体外循环和具有高液压的医疗器械。Jiang 等<sup>[96]</sup>采用疏水生物相容性聚己内酯 (PCL) 制备了电纺纳米纤维膜。将聚二甲基硅氧烷 (PDMS) 浸涂在 PCL 电纺膜上, 来制备超疏水 ECMO 膜, 改善了体外膜氧合 (ECMO) 系统长期应用中的血液相容性和气体交换效率。

### 3.3 伤口敷料

伤口愈合是全球数亿人面临的严重问题, 尤其是慢性伤口的愈合对患者和医疗系统都是挑战<sup>[97]</sup>。慢性伤口如糖尿病足、湿疹等, 在愈合过程中易发生感染, 而抗生素的过多使用促进了耐药菌的产生。此外普通的伤口敷料易黏附, 强行剥离可能导致撕裂、继发性出血和疼痛, 对血友病患者尤为危险。因此, 开发抗菌、抗粘连、快速止血的功能性敷料至关重要。超疏水材料具有抗粘连、抗菌、止血和促进伤口愈合的特性, 可赋予传统敷料不具有的功能, 因此在普通伤口治疗、手术切口、糖尿病足以及血友病伤口的护理中都有广泛的应用。Li 等<sup>[98]</sup>使用含有氟共聚物和季铵盐的季铵化聚合物 (PDMA-b-PFOEMA) 构建了超疏水涂层, 不仅具备抗菌功能, 还能具有抗粘连和快速止血功能, 这是由于超疏水性使血液在表面形成小水滴, 限制了其扩散, 并将血液集中在伤口部位, 从而加速凝血过程<sup>[99]</sup>。Li 等<sup>[100-101]</sup>用聚二甲基硅烷 (PDMS) 和氟化碳纳米管 (CNF) 制备了超疏水敷料, CNFs 能加速纤维蛋白快速凝聚, 防止血液流失, 并减少细菌附着。超疏水性质使血块在收缩后能够自然脱落, 从而使敷料易于移除, 避免二次出血的发生。凝血酶生成实验研究表明, 超疏水的 CNF 能通过激

活内在途径的第十二因子来促进快速的血液凝固<sup>[102]</sup>。Zhu 等<sup>[103]</sup>提出了超疏水/超亲水 Janus 织物的概念,该织物一方面具有超疏水性,另一方面则具有超亲水性。超亲水部分能够吸收血液中的水分,从而促进凝血,而超疏水部分可有效防止血液的进一步渗透。相较于普通敷料,Janus 织物能有效控制出血,减少超过 50% 的血液流失,同时保持良好的呼吸透气性,甚至延长了严重出血大鼠模型的存活时间。Long 等<sup>[104]</sup>创建了一种超亲水/超疏水交替内层和超疏水外层的不对称复合伤口纳米敷料 (ACWN) 的独特结构,通过大鼠实验,证明了内层 ACWN 具有良好的止血、抗粘连作用,并且超疏水的外层还可以防止血液外渗并降低感染的风险。Duan 等<sup>[105]</sup>设计了一种内表面为超疏水、中间层具有吸水能力的敷料,敷料表现出抗粘连特性,并且可以单向吸收伤口渗出物。

## 4 未来展望

超疏水涂层相比于普通的光滑表面在血液接触医疗器械表面的应用展现出了巨大的潜力,特别是在减少血栓形成和预防感染方面。这些涂层通过高表观接触角、低表面能量和复杂的表面结构,有效阻止了血液成分和细菌等有机物质的附着。虽然目前已有一些关于超疏水材料血液相容性的研究成果,并提出了若干作用机理,但由于血液成分复杂且多变,超疏水表面与血液的相互作用机制尚未完全阐明,这些效应通常交织在一起,使机制研究变得更加复杂。此外,现有的超疏水材料血液相容性研究多集中于体外实验,尚缺乏充分的体内研究。在实际的血流环境中,超疏水材料与血液的生物相容性仍需要进行更加全面和深入的评估。未来的研究方向应集中在以下几个方面:

首先是结合“直接成型”“自下而上”和“自上而下”3 种超疏水材料合成策略的优势,可以通过一步法或多步法开发出既具备良好血液相容性,又具备耐久性的超疏水表面,并确保其制备方法经济、适用且易于推广。在这一过程中,超疏水材料的微纳结构特征对表面保持 Cassie 状态具有重要影响,因此,借助人工智能技术深入探索超疏水表面特征与血液成分的相互作用机理,设计出具备良好生物相容性的超疏水材料,将是未来的发展方向之一。此外,超疏水材料的化学成分在体内的命运也是影响其生物相容性和应用的关键因素。因此,使用对人体无毒无害的材料(例如无氟类的低表面能物质)将是未来材料设计的重要考量。最后,超疏水材料在体内的长期稳定性和对细胞的生物安全性,尤其是其在实际临床应用中的生物安全性评价方法,仍需进一步完善和标准化。

综上所述,超疏水涂层作为未来血液接触医疗器械的潜在解决方案,虽然面临挑战和未解决的问题,

但在技术和研究上的持续推进将为其应用和发展提供广阔的前景。

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