类金刚石薄膜表面润湿调控研究综述

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摘 要：表面具有特殊润湿性特别是超疏水性的类金刚石薄膜，可满足在极端服役环境下（比如雨雪、潮湿环境中或者人体组织内）智能界面材料表面改性的需求。概述了类金刚石薄膜的生产工艺和性能优势及制备方法，介绍了具有特殊润湿性，特别是超疏水性的类金刚石薄膜的应用背景，同时提出了类金刚石薄膜表面润湿调控在理论和技术上的限制。在此基础上，阐述了类金刚石薄膜表面本征润湿性及与微观结构（包括杂化状态和短程或中程有序相团簇结构）间的关系。同时，基于经典的 Wenzel 和 Cassie 润湿理论，从表面化学组成和粗糙结构两个方面，重点论述了类金刚石薄膜表面润湿调控的方法及研究现状。通过等离子体表面处理、元素掺杂或者化学修饰改变 DLC 薄膜表面化学组成，实现 DLC 薄膜表面本征润湿改性。通过基体表面织构化或者薄膜表面形貌控制，构建 DLC 薄膜表面粗糙结构，控制界面润湿状态。二者共同作用可实现 DLC 薄膜表面润湿性在超亲水和超疏水之间变化。最后，总结并指出当前类金刚石薄膜表面润湿调控存在的一些关键科学问题，同时展望了未来的发展趋势。

关键词：类金刚石；润湿调控；化学组成；表面结构；超疏水性

中图分类号：TG174.4 **文献标识码：**A **文章编号：**1001-3660(2021)10-0147-10

DOI：10.16490/j.cnki.issn.1001-3660.2021.10.013

Review on Surface Wettability Regulation of Diamond-like Carbon Films

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ABSTRACT: Diamond-like carbon films with special surface wettability especially super-hydrophobicity can fulfill the demand of surface modification of smart interface materials serving under extreme conditions (e.g., in rain or snow weather, humid environment, or human body) in the fields of machine, electronic, optics and medicine, etc. Herein, the advantages of produce technique and performances and preparation methods of diamond-like carbon films were overviewed briefly. The application background of diamond-like carbon films with special surface wettability especially super-hydrophobicity was presented. Meanwhile, the limitations both in science and technique to freely regulate surface wettability of diamond-like carbon films were also proposed. In this context, the inherent surface wettability of diamond-like carbon films and its relations with microstructures (including hybridization state of carbon atoms and short or medium range ordered sp^2-C phase cluster structures) were demonstrated. Next, according to the classical Wenzel and Cassie wetting theories, a comprehensive review was

收稿日期：2020-10-13；**修订日期：**2021-02-18

Received：2020-10-13；**Revised：**2021-02-18

基金项目：内蒙古自然科学基金项目（2019LH05003）；内蒙古科技大学创新基金项目（2017QDL-B10）

Fund：Supported by the Natural Science Foundation of Inner Mongolia (2019LH05003), Innovation Fund Project of Inner Mongolia University of Science and Technology (2017QDL-B10)

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引文格式：孟可可，张中一，谭心．类金刚石薄膜表面润湿调控研究综述[J]．表面技术，2021，50(10)：147-156.

MENG Ke-ke, ZHANG Zhong-yi, TAN Xin. Review on surface wettability regulation of diamond-like carbon films[J]. Surface technology, 2021, 50(10): 147-156.

presented on the regulation methods mainly from two different aspects, i.e., surface chemical compositions and surface rough structures, and recent achievements on surface wettability regulation of diamond-like carbon films. On one hand, changing surface chemical compositions or surface free energy by plasma surface treatment, element doping or surface chemical modification could promote inherent surface wettability modification (i.e., hydrophilicity to hydrophobicity transition) of diamond-like carbon films. On the other hand, constructing specific surface rough structures on the micro/nano scales by substrate surface texturing or film surface morphology design would control the interface wetting state (e.g., Wenzel state, Cassie state or the transition state) of diamond-like carbon films. These two effects together gave rise to the variation of surface wettability of diamond-like carbon films between super-hydrophilicity and super-hydrophobicity. Finally, some key scientific issues that hinder the surface wettability regulation of diamond-like carbon films were proposed, and the research prospects and directions of this field were also briefly addressed.

KEY WORDS: diamond-like carbon; wettability regulation; chemical composition; surface rough structure; super-hydrophobicity

类金刚石（Diamond-like Carbon, DLC）是碳以 sp^2 和 sp^3 杂化键结合的一种非晶材料，兼具石墨和金刚石的优良特性，比如高硬度、高耐磨性、良好的透明性和生物相容性等，广泛用于机械、电子、光学和医学等领域[1-3]。1971 年，Asienberg 和 Chaboty[4]首次利用离子束沉积技术成功制备了 DLC 薄膜，因其性能优良且生产工艺简单，自此之后便在全世界范围内掀起了 DLC 薄膜的研究热潮。截至目前，人们已经开发出各种方法用于制备 DLC 薄膜，大体可以归为三类，即物理气相沉积[5-6]、化学气相沉积[5,7]和电化学液相沉积[8-9]。研究发现，采用不同方法或工艺制备的 DLC 薄膜的微观结构不同，造成 DLC 薄膜的各项性能出现显著差异，这为 DLC 薄膜的性能调控提供了理论和技术上的可能性。表面润湿性是 DLC 薄膜的重要基础性能之一。在一些特殊环境中，具有特殊润湿性能，特别是超疏水性（水接触角≥150°）的 DLC 薄膜可满足不同器件材料的特殊使用要求，比如机械器件表面防污和防腐[10-11]，光学器件表面防水、防雾和防冰[12]，医疗器件表面防血液和细胞粘附[13-15]等。然而，研究表明，DLC 薄膜表面本征亲水（水接触角<90°）[16]，而且表面粗糙度极小，很难满足特殊润湿性能，特别是很难满足超疏水性对表面本征疏水和复杂粗糙结构的要求。更重要的是，DLC 薄膜非晶态原子结构复杂多变，空间排布很难准确测定，薄膜表面本征润湿性与微观原子结构之间的内在联系仍存在较大争议，无法通过结构控制对 DLC 薄膜表面润湿性进行精准调控。因此，对 DLC 薄膜表面润湿调控的研究具有重要的理论和实际意义，不仅有助于深刻理解 DLC 薄膜表面润湿改性和调控机制，而且可为非晶碳膜制备技术在智能界面领域的进一步应用，提供坚实的理论和技术基础。

1 DLC 薄膜表面本征润湿性

微观上，固体表面润湿性即本征润湿性，是由界面固体原子与水分子间的耦合作用和氢键强度决定的[17]。所以，固体表面本征润湿性与固体表面原子结构或者表面能有关，其大小通常由液滴在光滑均质固体表面的静态接触角来表征。研究表明，DLC 的原子结构为在 sp^3 杂化碳（sp^3-C）空间网络中镶嵌着短程或中程有序的 sp^2 杂化碳（sp^2-C）团簇，其性质主要由 sp^2-C/sp^3-C 比值决定。sp^2-C/sp^3-C 比值越大，DLC 的性能就越接近石墨，反之则越接近金刚石。实验发现，金刚石(111)面和石墨(0001)面的水接触角分别为 35°和 80°[18]，均为亲水性表面。那么，由 sp^2-C 和 sp^3-C 组成的 DLC 薄膜表面润湿性应该介于石墨和金刚石之间，自然表现为亲水性。物理气相沉积 DLC 薄膜的表面润湿性见表 1。相对于化学气相沉积和电化学液相沉积，物理气相沉积 DLC 薄膜可以排除 H 元素对表面本征润湿性的影响。由表 1 可见，DLC 薄膜表面粗糙度极小（<30 nm），结构尺度远远小于水的毛细长度 2.73 mm，表面粗糙度对本征润湿性的影响可忽略不计，DLC 薄膜可近似认为是均质光滑固体表面。DLC 薄膜表面的水接触角为 54°~82°

表 1 物理气相沉积 DLC 薄膜表面粗糙度、表面能和水接触角

Tab.1 Surface roughness, surface energy and water contact angle of DLC films deposited by physical vapor deposition

Preparation method	Surface roughness/nm	Surface energy/(mJ·m^{-2})	Water contact angle/(°)	References
Filter cathode vacuum arc	0.08	42.8	77.6	[24]
Magnetron sputtering	—	—	54.0~64.0	[25]
Magnetron sputtering (*Ra*)	1.29	39.7	68.5	[20]
Magnetron sputtering	0.59~0.64	—	73.5~78.4	[26]
Magnetron sputtering (*Ra*)	4.40~23.50	34.0~43.7	57.6~82.0	[27]

（基本介于金刚石和石墨之间），不同方法制备的 DLC 薄膜均表现为本征亲水性。理论上，由于 sp^3-C 终止表面具有比 sp^2-C 终止表面更大的表面能[19]，所以 DLC 薄膜表面疏水性随着 sp^2-C/sp^3-C 比值的增加而增加[20]。然而，有学者在实验中却发现了截然相反的现象，即 DLC 薄膜表面疏水性随着 sp^2-C/sp^3-C 比值的增加而逐渐降低[12,21,22]。这一矛盾目前还没有得到合理的解释。另外，相关理论研究证明，DLC 薄膜表面能并不随 sp^2-C/sp^3-C 比值的增加而单调变化[23]。分析认为，这可能与不同杂化状态下，DLC 薄膜表面能的极性分量和色散分量的变化有关。另外，DLC 薄膜内短程或中程有序的 sp^2-C 团簇结构变化也需重点关注。

2　DLC 薄膜表面润湿调控

宏观上，固体表面润湿性即表观润湿性，由固体表面能或表面本征润湿性和表面粗糙度决定[28]。Wenzel 理论认为[29]，在均匀润湿状态下（均匀的固-液界面），表面粗糙度可放大固体表面本征润湿性，如图 1a 所示。Cassie 理论认为[30]，在复合润湿状态下（固-液和液-气复合界面），表面粗糙度始终增强固体表面疏水性，如图 1b 所示。固体表面处于何种润湿状态与表面本征润湿性和表面粗糙度的大小及结构形态密切相关[28,31]。基于以上理论，通过控制表面本征润湿性和表面粗糙结构，DLC 薄膜表面润湿性可以实现在超亲水和超疏水之间的变化。目前，DLC 薄膜表面润湿调控的方式有两种：一是改变表面化学组成，比如等离子体表面处理、元素掺杂、表面化学修饰等；二是构筑表面粗糙结构，比如基体表面织构化、薄膜表面形貌控制等。

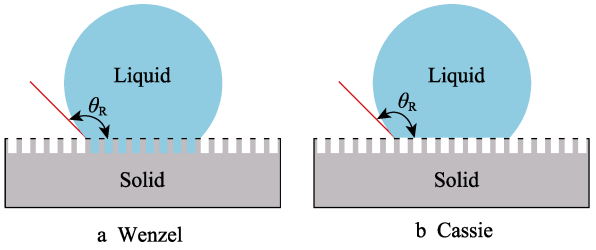


图 1　润湿状态示意图

Fig.1 Schematic illustrations of the (a) Wenzel and (b) Cassie wetting states

2.1　改变表面化学组成

2.1.1　等离子体表面处理

等离子体表面处理是固体表面改性的有效方法之一。通过对反应气体（比如 CF_4、H_2、O_2、N_2 或 NH_3 等）施加足够的能量，使之离化为等离子态，再利用这些活性组分轰击 DLC 薄膜表面，在表面形成极性或非极性官能团（比如—CF_x、—CH_x、—CO、—OH、—CN 等），进而对 DLC 薄膜的表面润湿性进行调控（见表 2）。曹伟[32]利用 CF_4 对非晶碳薄膜进行等离子体表面处理，使表面形成—CF_x 基团，降低表面能，提高薄膜表面疏水性。Artemenko 等[33]首先利用 O_2 对等离子体辅助化学气相沉积 DLC 薄膜进行等离子体刻蚀，薄膜表面水接触角由 27°降低到 9°，然后利用 H_2 对 O-DLC 薄膜进行等离子体处理，薄膜表面水接触角由 9°增加到 66°，最后利用 NH_3 对 H-DLC 薄膜进行等离子体处理，薄膜表面水接触角由 66°降低到 21°。等离子体处理纳米金刚石薄膜也表现出相似的表面润湿行为。Yun 等[34]分别利用 H_2 和 O_2 对射频等离子体化学气相沉积 DLC 薄膜进行等离子体处理，H-DLC 薄膜表面润湿性没有明显变

表 2　常见等离子体表面处理 DLC 薄膜表面润湿性比较

Tab.2 Comparison of surface wettability of DLC films treated by different plasmas

Preparation method	Plasma treatment	Water contact angle/(°)		References
		Before treatment	After treatment	
Magnetron sputtering	CF_4	105.0	151.0	[35-36]
PACVD		70.1±3.0	92.1±2.6	[37]
PECVD		70.0	135.0	[38]
RF-PECVD		83.0	135.0	[32]
Magnetron sputtering	H_2	152.0	<10.0	[35-36]
Magnetron sputtering +CF_4 plasma pretreatment		155.0	155.0	[35]
PACVD		70.1±3.0	42.1±6.0	[37]
Magnetron sputtering	N_2	152.0	<10.0	[35-36]
Magnetron sputtering +CF_4 plasma pretreatment		161.0	161.0	[35]
PACVD		70.1±3.0	42.7±3.7	[37]
RF-PECVD	O_2	65.4	11.1	[39]
PACVD		70.1±3.0	13.4±1.3	[37]

化，而 O-DLC 薄膜表面亲水性明显增强。分析认为，H 虽饱和了 DLC 薄膜表面悬键，但同时也增加了表面 sp^3-C 含量。Zhou[35]利用 N_2、H_2 对非晶碳和氟化非晶碳薄膜进行等离子体处理。结果发现，经等离子体处理后，非晶碳薄膜接触角由 152°减小至 30°以下，如图 2a 所示，而氟化非晶碳薄膜则表现出良好的稳定性，表面处理前后接触角几乎无变化，如图 2b 所示。

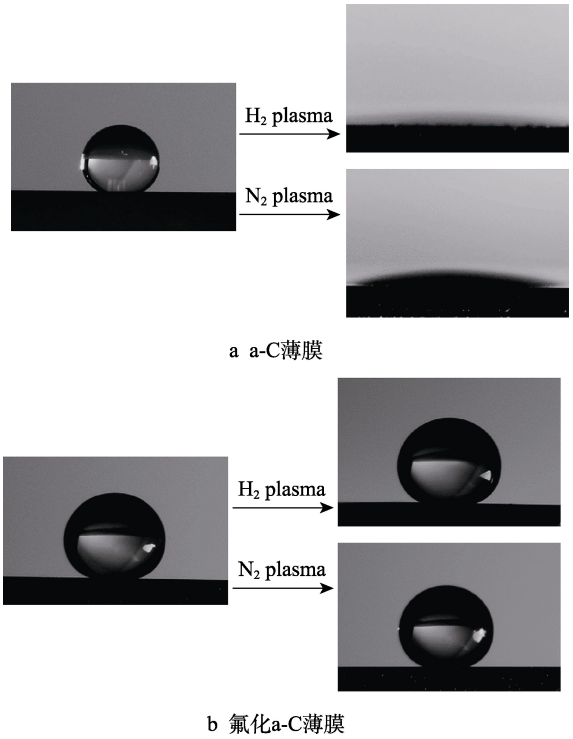


图 2　H_2 和 N_2 等离子体处理前后 a-C 和氟化 a-C 薄膜的表面润湿性变化[35]

Fig.2 Wetting variations of the (a) a-C and (b) fluorinated a-C films before and after H_2 and N_2 plasma treatment[35]

2.1.2　元素掺杂

2.1.2.1　非金属元素掺杂

H 是最常见的 DLC 薄膜非金属掺杂元素。H 原子掺杂在 DLC 中以—CH_x 形式存在，H 原子不仅能填补薄膜内部原子缺陷，还可以饱和表面悬键，降低表面能的极性分量，进而增强表面疏水性。相关研究表明[40]，H-DLC 薄膜表面疏水性与其 H 含量成正比。但是，掺杂 H 会导致 sp^3-C 含量增加，提高表面能的色散分量，进而降低表面疏水性。Shi 等[41]通过实验发现，磁控溅射沉积 DLC 薄膜掺杂 H 后，表面疏水性明显降低。在 DLC 薄膜中，掺杂 F 具有与掺杂 H 相似的作用，但由于 F-DLC 薄膜具有更低的表面能，所以掺杂 F 始终能增强 DLC 薄膜的表面疏水性[42]。Safaie 等[43]利用射频等离子体增强化学气相沉积法，制备了 O-DLC 薄膜。随着 O 浓度的提高，薄膜中 C═O 键和 C═C 键含量增加。由于 C═O 和 C═C 键比 C—C 和 C—H 键具有更高的极化率[44]，导致表面能增加，降低了水与薄膜的接触角。在 DLC 薄膜中掺杂 N[45]、P[46]与掺杂 O 类似，会导致表面能增加，表面疏水性降低。

Zhao 等[47]利用磁控溅射沉积技术制备了 Si-DLC 薄膜。随着 Si 含量的增加，sp^2-C 含量降低，Si—C 键增多，表面能的极性分量增加，水接触角降低。但也有报道称[48]，在氢化非晶碳膜中掺入 Si 元素，表面能从 43 mN/m 降低至 31 mN/m。表面能降低的主要原因是，氢化非晶碳网络中 sp^2-C 和悬挂键的减少，导致表面能极性分量降低。若 Si 和 O 共同掺杂可形成[$Si(CH_3)_3$-O-$Si(CH_3)_3$]单体，表面能进一步降低至 22 mN/m。Robertson 等[49]利用等离子体增强化学气相沉积技术，制备了 Ge-DLC 薄膜，表面极性 Ge—C 键的存在，导致表面能极性分量增加，表面接触角降低。

2.1.2.2　金属元素掺杂

金属元素与碳元素间不同键合作用（离子键、共价键、非键、反键）导致掺杂金属在 DLC 薄膜中的存在形式不同。其中，碳化物形成元素可以与碳原子发生化学键合，生成热力学稳定的硬质金属碳化物[50]，非碳化物形成元素不与碳发生键合反应，金属原子以纳米晶金属团簇的形态弥散分布于非晶碳基质中[51]。另外，与非金属元素掺杂类似，金属元素掺杂也会改变 DLC 薄膜中 sp^2-C/sp^3-C 比值。二者共同作用对 DLC 薄膜的表面润湿性进行调控。

2.1.2.3　碳化物形成元素

Chen 等[52]通过实验发现，非晶碳薄膜掺杂 Fe 后，表面由亲水性转变为疏水性。分析认为，薄膜中的 Fe 元素被氧化形成如(C_n—O—Fe)—O—(Fe—O—C_n)的氧化物网络，这些氧化物具有较少的不饱和键，偶极相互作用较弱，导致薄膜表面能的极性分量减小；同时，薄膜中 sp^2-C 含量的增加导致薄膜密度降低，使薄膜的色散分量减小。两者共同作用使薄膜表面能降低，疏水性能提高。但是，Ray 等[53]却得到了截然相反的结论。Jelinek 等[54]利用脉冲激光沉积和磁控溅射复合技术制备了 Cr-DLC 薄膜。随着 Cr 含量的增加，薄膜中 sp^2-C 含量增加，表面水接触角增大。与之不同的是，Dai 等[55]认为由于金属元素含量的增加以及表面粗糙度的降低，Cr-DLC 薄膜表面接触角随着 Cr 含量的增加而降低。综上，Fe 和 Cr 掺杂非晶碳薄膜表面润湿调控机理有待进一步深入研究。Sun 等[56]利用混合离子束系统制备了 W-DLC 薄膜。掺杂 W 可增加 sp^2-C 含量，降低表面能，但 W—C 键的形成又会消耗 sp^2-C，同时增加了表面偶极，致使表面能增加。因此，掺杂 W 对 DLC 薄膜表面润湿性的影响不大，仍然为亲水性，如图 3 所示。另外，DLC 薄膜中掺杂 Ti 可增强表面疏水性，掺杂 Nb 可降低表面疏水性[57]。

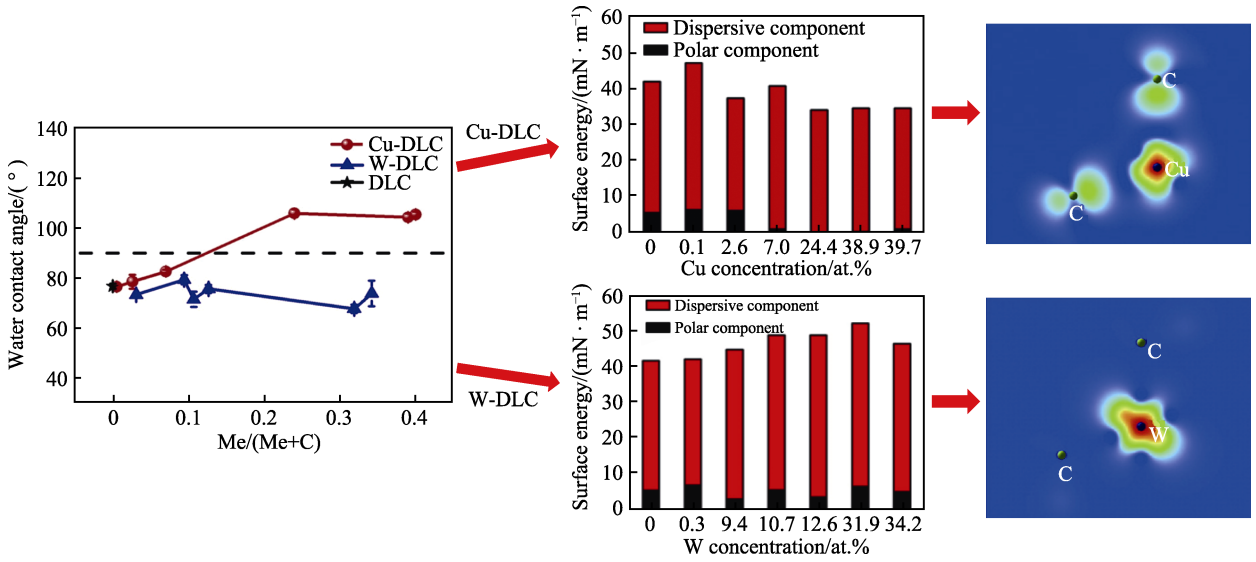


图 3　W-DLC 和 Cu-DLC 薄膜表面润湿性、表面能和电子结构[56]

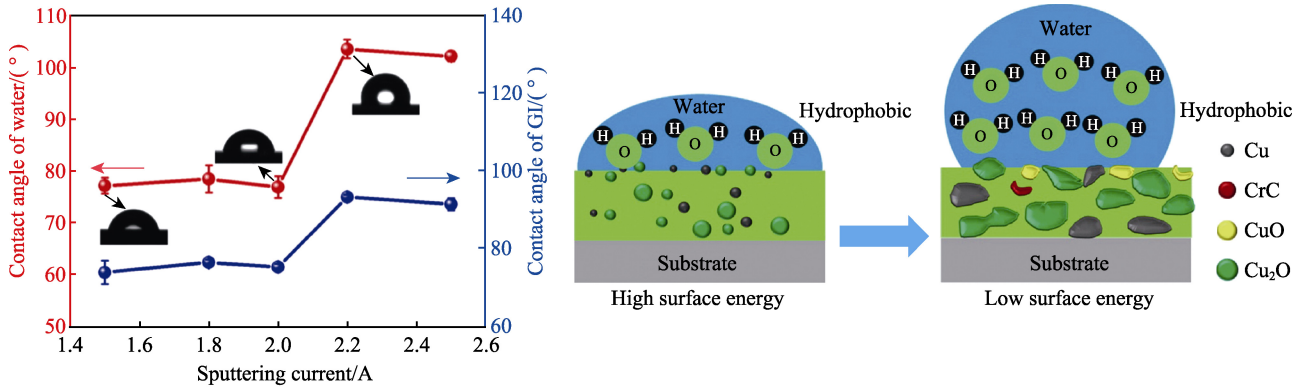
Fig.3 Surface wettability and surface energy of the W-DLC and Cu-DLC films with different metal concentrations and HOMO characteristics of W-C and Cu-C systems[56]

2.1.2.4　非碳化物形成元素

Sun 等[56]利用混合离子束系统制备了 Cu-DLC 薄膜。随着 Cu 含量的增加，薄膜中 sp^2-C 含量增加，表面由亲水性转变为疏水性。第一性原理计算结果显示，Cu 与 C 原子间为反键，Cu 在薄膜中以纳米晶团簇的形式存在，薄膜表面不存在永久偶极，表面能极性分量降低，如图 3 所示。在 DLC 薄膜中掺杂 Ag[58-60]和 Al[52,61]，表现出与 Cu 相似的疏水性能。Chen 等[52]利用过滤阴极真空电弧技术制备了四面体非晶碳（ta-C）和含 Ni 的非晶碳（a-C:Ni）薄膜，结果发现，ta-C 薄膜接触角为 77.6°，而 a-C:Ni 薄膜接触角为 68°。他们认为薄膜表面的镍只是部分被氧化，薄膜的极性分量增加，而色散分量保持不变，总表面能增加，接触角减小。

2.1.2.5　二元或多元共掺杂

随着 DLC 薄膜在各领域实际应用的不断深入，以特殊润湿为基础的薄膜表面多功能化需求越来越受到人们的关注。与单一元素掺杂不同，二元或者多元掺杂可以产生附加增强作用或者协同效应。因此，可以根据不同的应用需求选择两种或两种以上掺杂元素，同时优化 DLC 薄膜表面润湿性及其他相关性能。Sun 等[62]利用杂化离子束沉积系统制备了 Cu/Cr-DLC 薄膜，在增强 DLC 薄膜疏水性的同时，提高了薄膜硬度，并降低了内应力。不同溅射电流下 Cu/Cr-DLC 薄膜的表面润湿性和润湿状态演化示意图如图 4 所示。Swiatek 等[63]利用射频等离子辅助化学气相沉积制备了 Si/Ag-DLC 薄膜，同时增强了 DLC 薄膜的疏水性和抗菌性。Wu 等[64]利用磁控溅射技术沉积了 Cu/Ce-DLC 薄膜和 Cu/Ce/Ti-DLC 薄膜。由于 Ti 元素的引入，Cu/Ce/Ti-DLC 薄膜具有比 Cu/Ce-DLC 薄膜更强的疏水性能，同时耐腐蚀性能也得到了极大改善。



a 不同溅射电流下Cu/Cr-DLC薄膜表面润湿性　　b Cu/Cr-DLC薄膜表面润湿状态演化示意图

图 4　Cu/Cr-DLC 薄膜的表面润湿性和润湿状态演化示意图[62]

Fig.4 Schematic diagram of the evolution of surface wettability and wettability of Cu/Cr-DLC thin films[62]: a) wettability of Cu/Cr-DLC films under different sputtering currents; b) schematic illustration of the wetting state evolution of Cu/Cr-DLC films

2.1.3　表面化学修饰

表面化学修饰是通过表面化学反应引入表面官能团来改变固体表面能，并调控表面润湿性。Wei 等[65]首先对 Ti-DLC 薄膜进行 O 等离子体表面处理，表面接触角由 62°降低至~0°；然后在活性 Ti-DLC 薄膜表面自组装邻苯二酚，表面接触角由~0°增加至 34°；最后通过表面引发原子转移自由基聚合在初始修饰的 Ti-DLC 薄膜表面嫁接苯巯基尿酸，表面接触角由 34°降低至 7°。Nakamura 等[66]利用全氟辛烷光分解，在 DLC 薄膜表面引入全氟辛基官能团，氟基改性 DLC 薄膜表面接触角为 105°，与聚四氟乙烯相当，如图 5 所示。Nakamura 等[67]使用过氧化氢对 DLC 薄膜进行光化学修饰，表面形成含氧官能团。结果发现，氧基的引入增加了 DLC 薄膜表面亲水性。随后，将含氧 DLC 薄膜暴露在不同还原能力的氢化物还原剂中，作为控制 DLC 表面化学结构和表面润湿性的手段。使用 $LiBH_4$ 可以在表面形成羧基和羟基，表面接触角为 22°，而使用 $LiAlH_4$ 只能形成羟基，表面接触角为 44°，如图 6 所示。

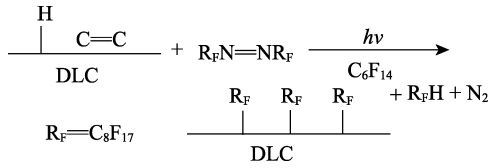


图 5　DLC 薄膜表面全氟辛基官能团化学修饰[66]

Fig.5 Surface chemical modification of DLC films with perfluorooctyl functional group[66]

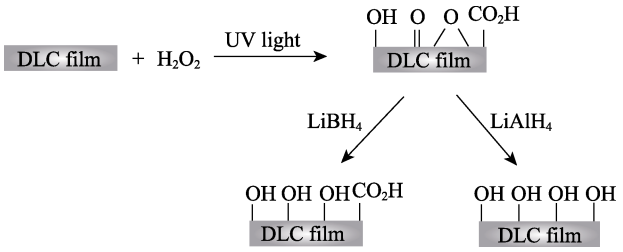


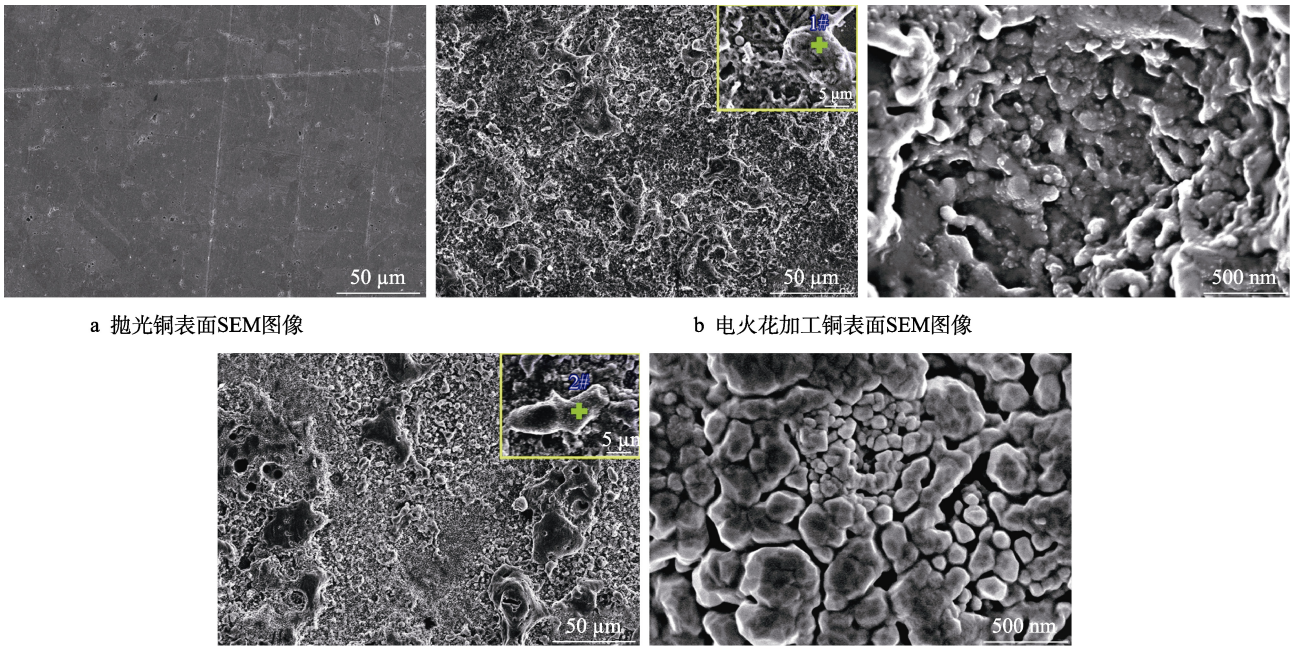
图 6　DLC 薄膜表面 H_2O_2 光化学修饰和氢化物还原[67]

Fig.6 Photochemical modification of DLC film with H_2O_2 and subsequent reduction with hydrides[67]

2.2　构建表面粗糙结构

2.2.1　基体表面织构化

在薄膜生长过程中，基体表面织构可以遗传下来，薄膜可获得与基体表面织构相似的表面形貌。He 等[68]在经电火花加工处理的铜表面沉积非晶碳薄膜，薄膜表面形成了微纳米分级乳突结构（见图 7），表面接触角高达 146.43°。Shum 等[69]在激光烧蚀铁表面沉积 DLC 薄膜，通过控制基体烧蚀结构，可以将 DLC 薄膜表面接触角由 68°提高到 130°。Kim 等[70]通过模仿荷叶，将疏水的 H、Si、O 掺杂非晶碳薄膜沉积在具有两级纳米粗糙结构的 Si 表面，获得了超疏水非晶碳薄膜，接触角高达 160°，接触角滞后<5°。王莹等[71]通过纳米铸造、电镀和物理气相沉积相结合的方法，成功制备出具有“荷叶”状纹理的 DLC 薄膜，接触角可达 160°。



a 抛光铜表面SEM图像　　b 电火花加工铜表面SEM图像

c 电火花加工铜表面沉积a-C薄膜SEM图像

图 7　电火花加工处理的铜表面沉积非晶碳薄膜[68]

Fig.7 Amorphous carbon film deposited on copper surface treated by EDM[68]: a) SEM images of polished Cu surface; b) EDM Cu surface; c) EDM Cu surface coated by a-C film

2.2.2　薄膜表面形貌控制

通过改变薄膜沉积参数，比如基体温度[16,32,36]、沉积功率[35-36,72-73]、沉积压力[73-76]、偏压[27,77]、时间[24,32,73]、气体流量比[32,78]、沉积电压[79]等，可以控制 DLC 薄膜表面形貌和粗糙度，进而实现对薄膜表面润湿性的调控。周英[36]通过调节磁控溅射温度，制备了具有显著表面形貌差异的非晶碳薄膜，其表面特征从光滑平坦过渡到具有丰富的孔隙和极其复杂的皱褶的分形结构，如图 8 所示，表面由强亲水性（接触角为 40°）转变为超疏水性（接触角为 152°）。通过调节磁控溅射功率在 Si 基体上沉积了具有类荷叶表面结构的非晶碳薄膜，薄膜与水接触角为 138°。另外，研究发现，增大沉积压力，可使光滑平坦 DLC 薄膜表面形成纳米或微米级球状颗粒[76]，甚至可以得到疏松粗糙的多孔结构[75]。随着偏压增大，非晶碳簇束的平均尺寸增大，簇束间距减小，薄膜表面形成微米级非晶碳簇束[77]。随着时间的增加，更多的含碳活性基团在碳颗粒团上继续聚集生长，并连续成膜，薄膜便快速地生长，直到趋向饱和，最后薄膜表面形成由许多弯曲的条状物杂乱排列而成的粗糙度很高的类似荷叶表面微观结构的纳米和微米二元稳定结构[32]。电化学沉积 a-C:H 薄膜由均匀分布且紧密排列的纳米颗粒组成，表面粗糙度较小[79]。这些结构使表面疏水性得到极大提高。气体流量组成对非晶碳薄膜表面形貌的影响比较小，导致对接触角变化也不明显[32,78]。因此，通过基体表面织构化和薄膜表面形貌控制，来构建 DLC 薄膜表面粗糙结构，改变表面润湿状态（Wenzel 状态、Cassie 状态或过渡态），可以实现对 DLC 薄膜表面润湿性的调控。

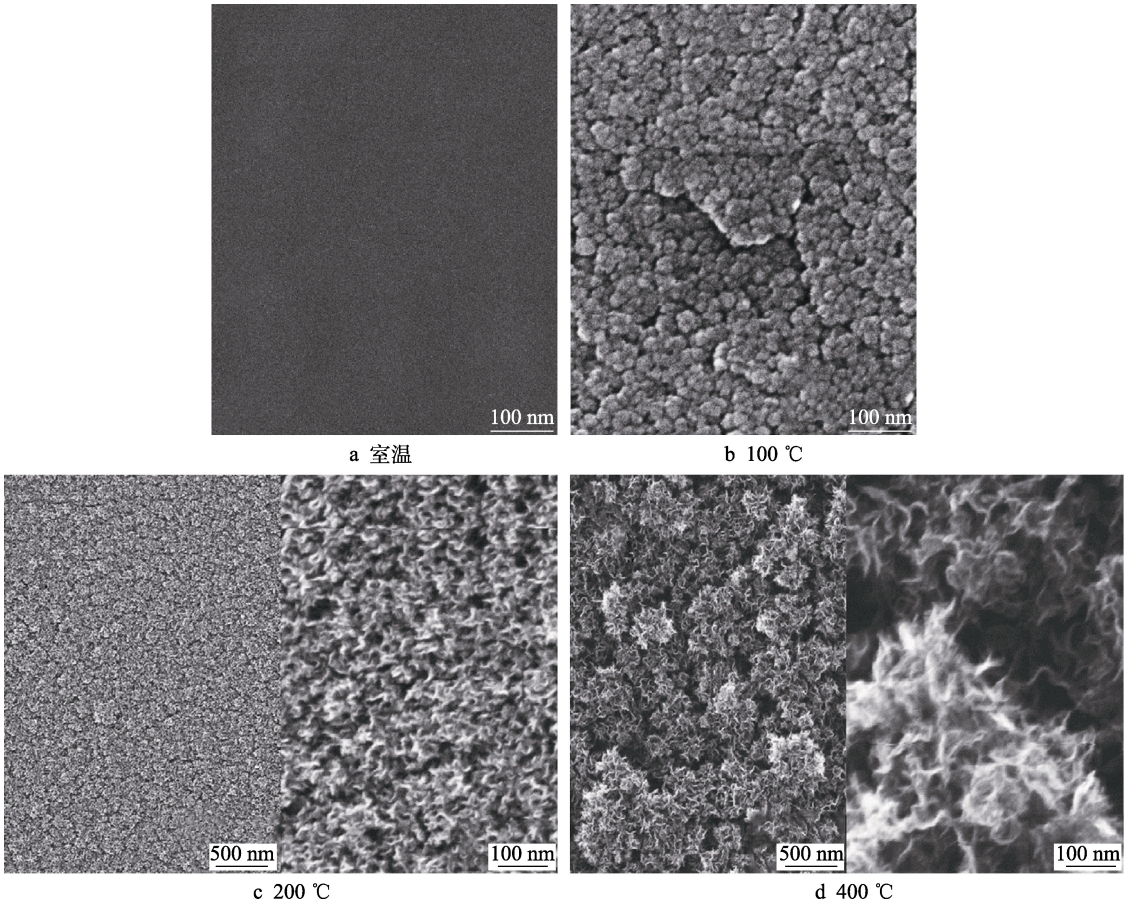


图 8　不同温度下的非晶碳薄膜 SEM 图像[36]

Fig.8 SEM images of the a-C films prepared under different temperatures[36]: a) room temperature

3　结论与展望

本文阐述了 DLC 薄膜表面本征润湿性及与微观结构之间的关系，并基于经典的 Wenzel 和 Cassie 润湿理论，从表面化学组成和粗糙结构两个方面，重点论述了 DLC 薄膜表面润湿调控的方法及研究现状。通过等离子体表面处理、元素掺杂或者化学修饰改变 DLC 薄膜表面化学组成，实现 DLC 薄膜表面本征润湿的改性；通过基体表面织构化或者薄膜表面形貌控制，构建 DLC 薄膜表面粗糙结构，控制界面润湿状态。二者共同作用可实现 DLC 薄膜表面润湿性在超亲水和超疏水之间变化。然而，尽管对 DLC 薄膜表面润湿调控的研究已经取得了一定的成绩，但仍然存在一些亟待解决的问题：

1）虽然针对 DLC 薄膜表面本征润湿性及与微观结构之间的关系开展了大量的研究工作，但有些结果

相互矛盾，需要结合分子动力学模拟，建立可靠的 DLC 薄膜原子结构模型，从原子尺度深入分析 DLC 微观结构演变对表面本征润湿性的影响。

2）需要进一步探讨 DLC 薄膜中相互交联碳基质网络的成键方式和 sp^2-C/sp^3-C 比值，特别是短程或中程有序 sp^2-C 相团簇结构对 DLC 薄膜表面能极性和色散分量的影响，并澄清掺杂诱导 DLC 薄膜表面润湿改性的物理机制。

3）合理评价超疏水 DLC 薄膜在极端服役环境中的机械稳定性和热稳定性，未来需要探索开发适用不同环境（温度、载荷等）的自适应、自修复超疏水 DLC 薄膜。

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