

化学气相沉积制备气凝胶研究进展

赵孔俐, 孙正阳, 冯军宗, 姜勇刚, 李良军, 胡艺洁, 冯 坚

(国防科技大学空天科学学院, 新型陶瓷纤维及其复合材料重点实验室, 长沙 410073)

摘 要: 气凝胶是一种具有低密度、高比表面积、低热导率等优异特性的纳米多孔材料, 在诸多领域应用广泛。但气凝胶传统制备工艺中凝胶化过程多在液相中进行, 凝胶干燥过程中为了避免受到表面张力的影响需要进行复杂的溶剂置换或使用专业的超临界干燥设备, 制备条件较为苛刻成本较高、制备工艺较为繁琐, 在一定程度上限制了其规模化应用, 而通过化学气相沉积工艺在气相环境中直接构造气凝胶纳米骨架可避免干燥步骤, 从而可大幅简化工艺流程并有可能降低其成本。同时, 采用化学气相沉积工艺制备的气凝胶具有良好力学性能并且此工艺更加适用于制备某些特殊结构的气凝胶。本文对气凝胶的化学气相沉积制备工艺包括无模板化学气相沉积法和模板辅助化学气相沉积法的最新研究进展进行了介绍, 并对未来研究方向进行了展望。

关键词: 气凝胶; 化学气相沉积; 模板法; 制备工艺

中图分类号: TQ170.1 文献标志码: A 文章编号: 0454-5648(2024)12-3896-09

网络出版时间: 2024-11-14



气凝胶是一种纳米量级粒子互相聚集构成纳米多孔网络结构, 并在空隙中充满气态分散介质的一种密度极低的高分散固体材料, 其具有高比表面积、高孔隙率、低热导率^[1]等特性, 在航空航天^[2]、建筑保温^[3]、能源材料^[4]、环境保护^[5]等领域具有广阔的应用前景。

目前, 气凝胶种类很多, 有无机气凝胶(氧化物陶瓷气凝胶(如 SiO_2 ^[6]、 TiO_2 ^[7]、 Al_2O_3 ^[8,9]等)、非氧化物陶瓷气凝胶(如 SiC ^[10]、 BN ^[11]等)、炭气凝胶^[12-15]、复相陶瓷气凝胶(如 $\text{Al}_2\text{O}_3\text{-SiO}_2$ ^[16]、 $\text{TiO}_2\text{-SiO}_2$ ^[17]等))、有机气凝胶(如聚酰亚胺^[18]、聚氨酯^[19]、纤维素^[20]等)、有机-无机复合气凝胶^[21-23]等。其中, SiO_2 气凝胶最具代表性, SiO_2 气凝胶通常采用溶胶-凝胶方法制备, 其工艺过程主要包括溶胶制备、凝胶老化和干燥 3 个主要步骤, 常使用硅醇盐作为主要原料, 水或者乙醇等作为溶剂在酸或者碱的催化下发生水解反应, 然后脱水缩合得到珍珠链状聚合物并形成水凝胶, 最后水凝胶经溶剂置换、干燥等步骤获得具有纳米量级连续网络结构的气凝胶, 过程如

图 1 所示。

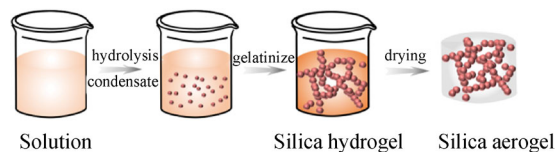


图 1 SiO_2 气凝胶传统液相制备工艺过程

Fig. 1 Conventional liquid phase preparation process of SiO_2 aerogel

与以上 SiO_2 气凝胶的制备方法类似, 氧化物气凝胶的制备一般选用醇盐作为原料, 利用溶胶-凝胶法在溶液内形成无序、枝状、连续网络结构的胶质颗粒, 并采用超临界干燥工艺去除凝胶内剩余的溶液而不改变凝胶态的结构, 该传统方法的主要特征是纳米三维网络结构是在液相中形成或构建, 需要通过干燥方式去除液相, 本文统称其为液相制备工艺。该类方法具有工艺成熟、应用广泛等优势, 然而在干燥过程纳米三维网络结构难以避免受到液体表面张力的影响。

与液相制备工艺相对应, 气凝胶化学气相沉积制备工艺是指在气相环境中直接生长或构建气凝胶

收稿日期: 2024-07-04。 修订日期: 2024-08-02。

基金项目: 国家自然科学基金(52302127)。

第一作者: 赵孔俐(2000—), 男, 硕士研究生。

通信作者: 冯军宗(1983—), 男, 博士, 副研究员。

Received date: 2024-07-04. Revised date: 2024-08-02.

First author: ZHAO Kongli (2000—), male, Master candidate.

E-mail: zkl0818@qq.com

Correspondent author: FENG Junzong (1983—), male, Ph.D., Associated Professor.

E-mail: junzongfeng@nudt.edu.cn

纳米三维网络结构的一种制备方法,按照是否需要模板可将此制备工艺分为 2 类:一是无模板化学气相沉积法和模板辅助化学气相沉积法,其主要特点为气凝胶制备过程中纳米骨架不在液相中生成,制备过程不需要干燥,能够有效避免传统液相溶胶-凝胶法干燥过程中表面张力对纳米骨架的影响,可利于气凝胶的高效、低成本制备^[24],并且通过化学气相沉积工艺制备的部分气凝胶具有更加优异的力学性能(如可压缩性能^[25-27]、负泊松比^[28]等);二是此工艺还可以通过模板辅助精细定制碳化硅、氮化硼气凝胶的微观结构以提升材料的某些性能^[29-31]。因此,化学气相沉积工艺是一种具有发展潜力的气凝胶制备工艺,

本文主要针对气凝胶化学气相沉积制备工艺,分别就无模板化学气相沉积法和模板辅助化学气相沉积法 2 种方法的研究进展进行总结分析,并对未

来的发展方向进行了展望。

1 无模板化学气相沉积法

无模板化学气相沉积法是一种高效(制备周期通常少于 1 d,如表 1 所示)制备气凝胶材料的技术,主要指利用气相碳/硅源(如丙烷^[24]、甲烷^[32]、乙炔^[33]和氧化硅气体^[27]等)在具有活性位点的基材或浮动催化剂^[34]上进行反应,生长出各种纳米结构单元,如珍珠链状^[24]、纳米线状^[25,27,35-36]和纳米管状^[32,37-42]等,随着纳米单元数量的不断增加,它们通过自组装的方式相互连接,最终构建成独特的气凝胶结构。此方法制备的气凝胶的微观结构和宏观形貌直接受到纳米单元形态和组装方式的影响,故通过调控纳米单元形态和组装策略可以制备出不同类型的气凝胶材料,包括气凝胶块体和气凝胶纤维。表 1 汇总了

表 1 无模板化学气相沉积法制备气凝胶的相关参数及材料性能

Table 1 Parameters and material properties of aerogels prepared by template-free chemical vapor deposition method

Target aerogel	Raw materials	Temperature/℃	Time/h	Density/(g·cm ⁻³)	S _{BET} /(m ² ·g ⁻¹)	Thermal conductivity/(W·m ⁻¹ ·K ⁻¹)	Mechanical property	Reference
SiC	Siloxane xerogel	1 450	2	0.005	78.00	0.026(26 ℃)	1 000 cycles (ε:40%)	[27]
SiC	CaCO ₃ , C SiO ₂ , Si	1 500	7	~0.009	163.85	0.020(26 ℃)	6% deformation 100 cycles(ε:60%) slight deformation	[25]
SiC	CaCO ₃ , C SiO ₂ , Si	1 500	5	0.011	—	0.027(26 ℃) 0.041(200 ℃) 0.069(400 ℃) 0.105(600 ℃) 0.035(26 ℃)	1 000 cycles(ε:60%) slight deformation	[26]
SiC	CaCO ₃ , C SiO ₂ , Si	1 400	2	0.004	—	0.041(100 ℃) 0.067(300 ℃) 0.125(500 ℃)	100 cycles(ε:40%) 5% deformation	[35]
SiC	Si, SiO ₂ C	1 400	2	0.036	—	0.020(26 ℃) 0.055(500 ℃)	—	[36]
Carbon	Propane Ar	950–1 000	5	0.12	12.80	0.049(26 ℃)	0.543 MPa (Compressive strength)	[24]
Carbon	Acetylene Ar, H ₂ CH ₄	700	—	—	365.00	—	—	[33]
Carbon	H ₂ , Ar Ferrocene Thiophene H ₂ , N ₂ Ferrocene	1 200	<1	0.032– 0.055	170.00	0.127–0.137 (26 ℃)	—	[32]
Carbon	Nickelocene Cobaltocene Thiophene C ¹³ H ₄ , ethanol, toluene	700–1 250	—	—	—	—	—	[41]
Carbon	H ₂ , Ar Ferrocene Thiophene Waste engine oil	1 200	—	—	—	—	—	[40]
Carbon	Ferrocene Thiophene Ethanol	1 150	—	—	142.90	—	—	[37]
Carbon	Ferrocene Thiophene Ethanol	1 250	<1	—	395.00	—	308.56 MPa (Tensile strength)	[38]
Carbon	Ferrocene Thiophene Acetone	1 000	<1	—	—	—	—	[39]
Carbon	H ₂ , Ar Ferrocene Thiophene	1 200	—	—	—	—	—	[42]

无模板化学气相沉积法制备气凝胶的工艺参数以及对应材料的性能数据。

1.1 无模板化学气相沉积法制备气凝胶块体

无模板化学气相沉积法制备气凝胶块体是在基材上生长纳米线状或珍珠链的纳米单元,并使这些纳米单元以相互缠绕或堆叠的方式构筑出气凝胶块体,此种组装方式目前可用于制备碳化硅纳米线气凝胶块体^[25,27,35–36]和炭黑气凝胶块体^[24],其基本技术路线为:首先通过加热 C/CaCO₃和 Si/SiO₂粉末或硅氧烷干凝胶等原料,释放出作为碳源和硅源的 CO 和 SiO 气体;随后, SiO 气体与基材表面的活性位

点发生反应,形成碳化硅晶核;在 1 400~1 500 ℃ 的高温条件下, SiO 和 CO 持续反应使碳化硅晶核生长为纳米线,并最终组装成气凝胶块体。分离产物与基材并经热处理去除杂质后,即可获得纯净的碳化硅纳米线气凝胶(见图 2);炭黑气凝胶的基本技术路线与上述碳化硅纳米线气凝胶相似故不再赘述。在整个反应过程中,基材的重要作用在于提供初始的活性位点以启动化学反应,而后续 SiO 和 CO 气体以适当比例连续反应[式(1)],则是确保碳化硅纳米线能够连续生长并形成完整块体的关键所在。

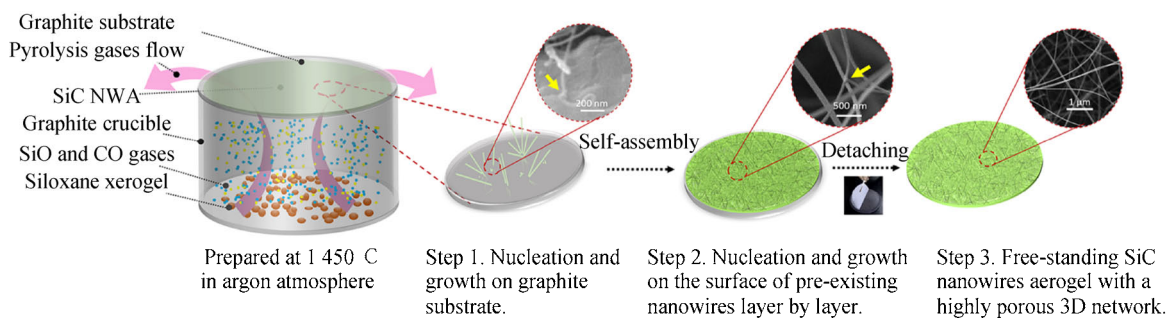
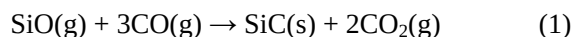


图 2 无模板化学气相沉积法制备气凝胶块体生长过程^[27]

Fig. 2 Growth process of aerogel prepared by template-free chemical vapor deposition^[27]

采用无模板化学气相沉积法制备碳化硅纳米线气凝胶时,后续生成的纳米线可以在先前存在的纳米线表面上成核并生长,纳米线之间得以结合牢固不易被外力破坏,加之一维碳化硅纳米线具有优异弹性、柔韧性和高拉伸强度^[43–44],因而此方法制备的碳化硅纳米线气凝胶整体具有良好的可压缩性能。Su 等^[27]最先使用化学气相沉积方法制备陶瓷气凝胶,通过加热硅氧烷干凝胶产生 SiO 和 CO 气体,然后使其在高温下持续反应[式(1)],从而在气相环境中生长出大量直径为 20~50 nm、长度为数 10 至数百 μm 的碳化硅纳米线,最后这些碳化硅纳米线以相互交织搭接的方式组装成三维碳化硅纳米线气凝胶,其以 60% 的形变量、加载率为 80 mm/min 的条件承受 1 000 个加载卸载疲劳循环后形变量仅为 6%,还具有优异的耐高温、隔热、抗氧化性能,因此在热防护和有机物吸附等领域具有广阔的应用前景。

同时,无模板化学气相沉积法是一种方便、简单、高效的纳米纤维陶瓷气凝胶制备方法^[45],Song 等^[25]在 7 h 内以炭粉/碳酸钙为碳源,硅粉/二氧化硅混合粉末为硅源,通过马弗炉简单加热在石墨坩埚中生长出大量直径为 200~400 nm、长度为数数百 μm

的碳化硅纳米纤维,这些碳化硅纳米纤维相互缠绕,形成结构稳定、三维互连的多功能碳化硅纳米纤维气凝胶,其具有相当低的密度(0.009 g/cm³)、优异的机械性能、良好的高温热稳定性和良好的隔热性能,还具有卓越的吸波性能(材料厚度为 1.9 mm 时,电磁波频率为 7.0 GHz 时的最小反射损耗值为-39.4 dB)。

无模板化学气相沉积法还可以在一定程度上调控纳米线的微观结构,Wang 等^[35–36]通过控制原料比例和高温氧化 2 种方式调控碳化硅纳米线表面 SiO₂ 壳层的厚度,以增强碳化硅纳米线气凝胶的介电损耗能力,其吸波性能因而得以强化,最小反射损耗值低至-57.2 dB,有效吸收带宽可达 9.4 GHz(8.6~18.0 GHz),同时还具有良好高温稳定性,在高温吸波领域表现出了较大应用潜力。

使用此方法也可高效制备炭气凝胶。Zhou 等^[24]采用与致密 C/C 复合材料制备^[46–47]相近的化学气相沉积工艺,以甲烷为主要碳源,首先高温加热使甲烷分解成小分子活性单元(如烃基),然后小分子活性单元在气相环境中不断碰撞脱氢形成炭黑颗粒,最终这些炭黑颗粒通过堆积的方式在碳毡内部构筑了三维多孔的炭黑气凝胶,其具有良好的隔热性能

(热导率为 $0.049 \text{ W/(m}\cdot\text{K)}$)和疏水性能(疏水角为 152.1°),同时制备时间仅需几个小时,此外,由于沉积是在纤维预制体的内部进行也可称此方法为化学气相浸渍^[48]。Acauan 等^[33]使用表面活化后的铜板作为基底提供化学气相沉积所需的初始活性位点,在 700°C 生长无定型炭纳米纤维,不断相互缠绕并紧密堆积制得具有相对较高比表面积($365 \text{ m}^2/\text{g}$)的炭气凝胶。

目前采用无模板化学气相沉积法制备的碳化硅气凝胶块体具有良好的可逆压缩性、弯曲性能、高温稳定性和吸波性能;制备的炭气凝胶块体具有优异隔热性能和疏水性能且制备用时较短。但是,受限于所用基体,制备大型碳化硅气凝胶构件可能较为困难。

1.2 无模板化学气相沉积法制备气凝胶纤维

无模板化学气相沉积法制备气凝胶纤维主要通过浮动化学气相沉积制备碳纳米管并进行纺丝使碳纳米管定向排列进而组装成气凝胶纤维的工艺方法,该方法能够在宏观尺度上保留碳纳米管的一些重要特性。目前该方法仅见于制备碳纳米管气凝胶,这种气凝胶最初是由 Li 等^[49]提出,目前,大多数碳纳米管气凝胶的研究都集中在如何将碳纳米管纳米尺度上优异力学性能和电性能传递到宏观尺度样品上^[34]。

浮动化学气相沉积与传统化学气相沉积相近,

主要区别在于浮动化学气相沉积不需要沉积基材,反应所需的活性位点由气态催化剂提供。其装置通常由 4 个主要部分组成:加热单元,前驱体净化组件,气体供应单元,收集单元;制备原料主要有:碳源(甲烷^[41,50]、乙醇^[38-39]、丙酮^[42]等),催化剂(二茂铁^[32,37-42]、二茂钴^[41]、二茂镍^[41]),促反应剂(噻吩^[32,37-42]),载气(氢气、氩气)。通过浮动化学气相沉积制备碳纳米管气凝胶的基本路线为:首先将含有碳源、催化剂和促反应剂的前驱体溶液预热,产生的前驱体蒸汽经过净化后被吹扫器吹扫随载气进入炉内,中心线温度保持在 $1000\sim 1500^\circ\text{C}$ 以使反应顺利进行,使用位于炉管出口处的旋转棒收集反应过程中产生的碳纳米管气凝胶纤维(如图 3 所示)。此方法生产的碳纳米管气凝胶纤维力学性能和电性能良好,拉伸强度为 $(308.56\pm 24.6) \text{ MPa}$,最大电导率为 $(1.02\pm 0.19) \text{ MS/m}$,较好的保持了碳纳米管的微观特性^[38]。但是,目前浮动化学气相沉积法制气凝胶纤维可重复性相对较差,碳纳米管气凝胶的一些优异性能难以完美复现。

无模板化学气相沉积法制备气凝胶无需干燥步骤、材料性能优异等优点,且制备周期远短于传统液相方法。但是目前还存在一些不足,可通过无模板化学气相沉积法进行制备的气凝胶种类较少,就目前的报道来看,此方法主要用于制备部分炭材料气凝胶和碳化硅气凝胶。

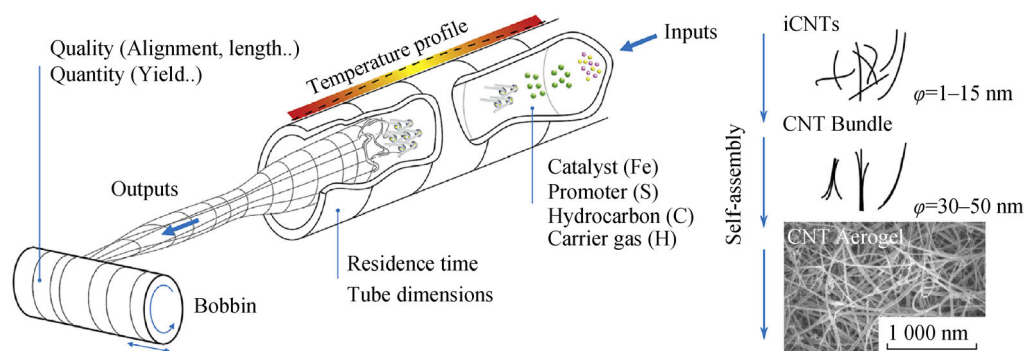


图 3 无模板化学气相沉积法制备气凝胶纤维生长过程^[51]

Fig. 3 Growth process of aerogel fibers prepared by template-free chemical vapor deposition method^[51]

2 模板辅助化学气相沉积法

模板辅助化学气相沉积法相较上述无模板方法最大区别在于:无模板化学气相沉积法主要在基材上生长纳米单元并以此构筑气凝胶,形貌取决于纳米单元的组装方式;而模板辅助化学气相沉积法主要在模板的纳米骨架上发生少量沉积,形貌主要取

决于模板,在一定程度上可按需设计气凝胶的微观结构。按照化学气相沉积反应过程中气体是否与模板发生反应可将模板辅助化学气相沉积法分为惰性模板辅助化学气相沉积法和活性模板辅助化学气相沉积法 2 类。表 2 汇总了模板辅助化学气相沉积法制备气凝胶的工艺参数以及对应材料的性能数据。

表 2 模板辅助化学气相沉积法制备气凝胶的相关参数及材料性能

Target aerogel	Raw materials	Templates	Time/h	Density/(g·cm ⁻³)	S _{BET} /(m ² ·g ⁻¹)	Thermal conductivity/(W·m ⁻¹ ·K ⁻¹)	Mechanical property	Reference
BN	B ₂ O ₃ , N ₂	Activated carbon	0.75	0.270	167.80	—	—	[52]
BN	B ₂ O ₃ , N ₂	Graphene aerogel	—	—	431.00	—	—	[53]
BN	Borazine	Graphene/CNT aerogel	0.5–2	0.001	1 051.00	—	—	[54]
BN SiC	Borazine Hydridopolycarbosilane	Graphene aerogel	3.3	0.000 1	1 080.00	0.020(26 °C) 0.002(vacuum)	Superelasticity up to 95%	[28]
Carbon	CH ₄ H ₂ , Ar	SiO ₂ aerogel	—	0.002	970.00	—	Support a weight of 200 g (Own weight of 4.8 mg)	[29]
Carbon	CH ₄ H ₂ , Ar	SiO ₂ aerogel	—	—	1 590.00	—	Support over 10 000 times its own weight	[30]
BN	B ₂ O ₃ , N ₂	GO/CNT aerogel	—	0.001	716.56	—	—	[55]
SiC	Polycarbosilane	Carbon foam loaded with Ni ²⁺	6	~0.030	—	0.030(26 °C) 0.230(900 °C)	0.11 MPa (Compressive strength)	[56]
SiC	Si@SiO ₂ nanoparticles	GO aerogel	1–5	—	—	0.020(26 °C) 0.031(400 °C) 0.051(800 °C) 0.118(1 200 °C) 0.026(26 °C)	100 cycles(ε:60%) 4% deformation	[57]
SiC	Si@SiO ₂ nanoparticles	SA _{nw} /GO aerogel	5	~0.010	179.60	0.039(200 °C) 0.065(400 °C) 0.098(600 °C)	100 cycles(ε:60%) slight deformation	[31]

2.1 惰性模板辅助化学气相沉积法

惰性模板辅助化学气相沉积法主要指以具有气凝胶结构的材料为模板，采用化学气相沉积的方法在其纳米骨架上生长所需材料且不与模板发生反应，然后采用热刻蚀或者化学刻蚀去除固态模板后得到与模板具有相似微观形貌的气凝胶。因此，其最大优势是能够根据模板结构定制所需气凝胶的结构。

惰性模板辅助化学气相沉积法的制备过程大致分为 3 个过程：制备模板、气相沉积以及去除模板(见图 4)，其中模板的制备与选择最为重要，在一定程度上决定了气凝胶的最终性能，所需模板不仅需要具有纳米三维多孔结构，还要考虑模板是否容易去除这一因素，常用的惰性模板有氧化硅气凝胶^[29–30]和石墨烯–碳纳米管复合气凝胶^[54]。

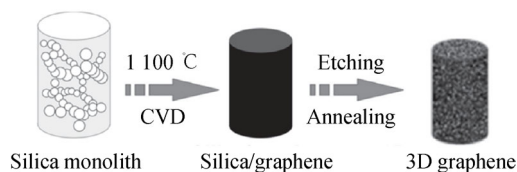


图 4 惰性模板辅助化学气相沉积制备石墨烯气凝胶过程^[29]
Fig. 4 Process of graphene aerogel prepared by inert template-assisted chemical vapor deposition^[29]

Huang 等^[29–30]选用 SiO₂ 气凝胶为模板，制备了具有四面连通的空心管状石墨烯气凝胶，其具有极

高强度(可支撑自身 40 000 倍的质量)和超高弹性(1 000 次 80%~90%压缩循环后最大应力保留超过 80%)。另外，该团队通过在四面连通的空心管内填充石墨烯获得了具有特殊多级结构石墨烯气凝胶，这种材料具有高比表面积(1 590 m²/g)和高导电率(32.5 S/cm)等特点，作为储能器件时具有 303 F/g 的高比电容且 10 000 次循环后保持率超过 98%，在能源领域具有较大的应用潜力。Song 等^[54]以石墨烯–碳纳米管复合气凝胶为模板，制备了超轻氮化硼气凝胶，其密度低至 0.005 g/cm³，同时好具有较高的比表面积(1 051 m²/g)和良好吸附能力(可吸收自重 160 倍的油)，这些特性使其在水体净化和环境保护等领域具有较大应用潜力。

2.2 活性模板辅助化学气相沉积法

活性模板辅助化学气相沉积法是指在高温环境中使气相原料进入纳米三维多孔模板中并与模板组分发生原位替代(如图 5 所示)，进而得到所需气凝胶。Han 等^[52]报道了以多孔活性炭为模板，以氮气和氧化硼为氮源和硼源，在高温下合成出多孔氮化硼气凝胶的方法，合成的氮化硼气凝胶拥有与模板活性炭相似的多孔结构，但是由于活性炭孔结构不够均一且先驱体在固体多孔模板中填充不充分，氮化硼气凝胶比表面积远低于活性炭模板的比表面积。Kutty 等^[55]以氧化石墨烯–碳纳米管气凝胶为活

性模板,在高温下通入氮气和氧化硼发生原位替代,制得高比表面积($716.56 \text{ m}^2/\text{g}$)的氮化硼气凝胶。此外,通过改变气体原料比例、温度等条件有可能实现原子不完全取代制备出含氮、硼、碳 3 种元素的气凝胶材料。

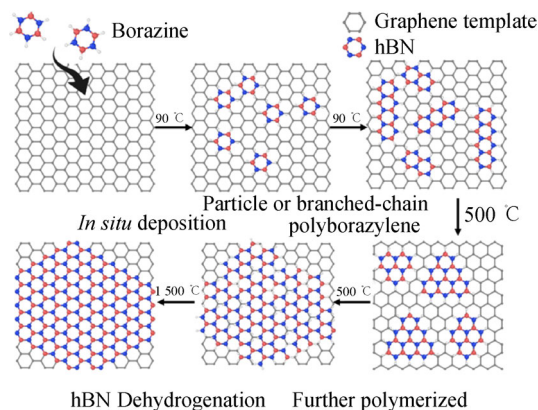


图 5 活性模板辅助化学气相沉积反应机制^[28]

Fig. 5 Reaction mechanism of reactive template-assisted chemical vapor deposition^[28]

采用模板辅助化学气相沉积法可降低制备特殊结构氮化硼气凝胶的难度, Xu 等^[28,58]首先制备出具有负 Poisson's 比和负热膨胀系数的双曲线型多孔石墨烯气凝胶模板,然后通过活性模板辅助化学气相沉积制备了具有负 Poisson's 比和负热膨胀系数的氮化硼气凝胶,该气凝胶孔隙率高达 99.99%,密度仅为 0.0001 g/cm^3 ,另外,负 Poisson's 比使氮化硼气凝胶具有良好的机械性能和超弹性,弹性应变高达 95%。

石墨烯气凝胶等纳米多孔炭材料不仅可作为制

备氮化硼气凝胶活性模板,同样可作为制备碳化硅气凝胶的活性模板,其原理为:气相硅源(气态 SiO ^[31,57])进入多孔结构中并与碳组分发生反应生成碳化硅,继承原有模板的纳米多孔结构,进而得到气凝胶。

一维碳化硅纳米线和二维碳化硅纳米片的组合结构可以实现良好的阻抗匹配,但是这种特殊的碳化硅纳米结构难以通过液相方法直接合成,而一维碳纳米线和石墨烯的组合结构相对容易合成, Song 等^[31,57]首先制备出一维纳米线和二维纳米片组成海藻酸钠纳米线-氧化石墨烯复合气凝胶模板,在 1350°C 气态 SiO 进入模板内部与碳组分发生反应生成碳化硅,此方法制备的碳化硅气凝胶较好地继承了模板的结构,因此,该碳化硅气凝胶的纳米结构由一维碳化硅纳米线和二维碳化硅纳米片组成,这种结构能够实现较为理想的阻抗匹配,从而使材料具有良好的吸波性能,反射损耗可达 -61.6 dB ,最大有效吸收带宽为 9.8 GHz 。

对比于气凝胶的液相制备方法,模板辅助化学气相沉积法更加适用于合成具有特殊结构气凝胶,如空心管状石墨烯气凝胶、双曲线型多孔氮化硼气凝胶、碳化硅纳米线-碳化硅纳米片复合气凝胶等难以通过液相方法合成的气凝胶。但是,该方法对模板要求较高,通常需要专门制备,材料整体的制备流程较长,从产业化角度进行分析,也不够节能。

无模板化学气相沉积和模板辅助化学气相沉积既有相似之处,也有不同之处,表 3 对比了无模板化学气相沉积和模板辅助化学气相沉积的工艺、性能、应用领域、优缺点等。

表 3 无模板化学气相沉积和模板辅助化学气相沉积的对比

Table 3 Comparison of template-less chemical vapor deposition and template-assisted chemical vapor deposition

Items	Template-free chemical vapor deposition	Template-assisted chemical vapor deposition
Preparation mechanism and process	Growth of various nanostructured units on substrates with active sites, interconnected to build aerogels	Using a material with an aerogel structure as a template to grow the desired material on its nanoskeleton
Applicable material scope	SiC nanowire aerogel, carbon aerogel, etc	BN aerogel, SiC aerogel, Graphene aerogel, etc
Aerogel characteristics and properties	low density, excellent mechanical properties, good thermal stability at high temperatures and good thermal insulation properties, etc	Negative Poisson's ratio, good wave absorption, high specific capacitance, etc
Field of application	Thermal protection, organic adsorption, electromagnetic wave absorption, etc	Energy storage, water purification, environmental protection, thermal protection, etc
Advantages and disadvantages	Preparation time is relatively short, but the preparation of large SiC aerogel building blocks may be difficult due to the substrate used	More suitable for synthesizing aerogels with special structures, however, the method usually requires specialized preparation of templates and may not be energy enough efficient

3 总结与展望

本文对化学气相沉积制备气凝胶的近期研究进展进行了总结。气凝胶化学气相沉积制备工艺中的

无模板化学气相沉积法可制备出性能优异的炭材料气凝胶和多功能碳化硅纳米线气凝胶,同时制备周期仅需几小时;模板辅助化学气相沉积法可根据模板定制气凝胶的微观结构以实现一些特殊功能(如

超弹性、负 Poisson's 比等)。由于不存在液相, 化学气相沉积工艺制备气凝胶可完全避免干燥过程表面张力的影响, 制备过程更加高效, 但是相比于传统气凝胶液相制备工艺, 其在相关领域的研究还不够充分, 针对目前存在的问题, 后续可能的研究方向包括:

1) 进一步简化工艺流程。气凝胶化学气相沉积制备工艺中的模板辅助化学气相沉积法通常需要专门制备具有气凝胶结构的模板, 增加了工艺的复杂度, 不利于规模化生产。工业生产的气相氧化硅或气相氧化铝具有与气凝胶相似的结构, 采用气相氧化硅或气相氧化铝作为模板, 在其纳米骨架上生长所需材料, 有望降低部分氧化物气凝胶的制备成本。

2) 开发条件更加温和的气凝胶化学气相沉积制备工艺。目前, 采用化学气相沉积制备气凝胶时, 反应温度大多超过 1 000 °C。可通过引入催化剂等方法使反应所需条件更加温和, 降低对设备的要求, 这可能是气凝胶化学气相沉积工艺未来发展的一个重要方向。

3) 拓宽气凝胶化学气相沉积工艺的材料种类适用范围。基于目前报道, 可采用化学气相沉积工艺进行制备的气凝胶种类较少, 主要是炭材料、碳化物、硼化物等气凝胶, 通过深入探究气凝胶化学气相沉积制备工艺的反应机理, 有可能将化学气相沉积工艺应用于氧化物(如氧化硅、氧化铝)气凝胶的制备, 从而进一步发挥化学气相沉积制备工艺周期短、无需干燥的优势。

参考文献:

- [1] GUO J R, FU S B, DENG Y P, et al. Hypocrystalline ceramic aerogels for thermal insulation at extreme conditions[J]. *Nature*, 2022, 606(7916): 909–916.
- [2] JIN R Z, ZHOU Z H, LIU J, et al. Aerogels for thermal protection and their application in aerospace[J]. *Gels*, 2023, 9(8): 606.
- [3] BERARDI U, SPRENGARD C. An overview of and introduction to current researches on super insulating materials for high-performance buildings[J]. *Energy Build*, 2020, 214: 109890.
- [4] SHEN J, ZHANG X X. Recent progress and applications of aerogels in China[J]. *J Sol Gel Sci Technol*, 2023, 106(2): 290–318.
- [5] WU Z Y, LIANG H W, CHEN L F, et al. Bacterial cellulose: A robust platform for design of three dimensional carbon-based functional nanomaterials[J]. *Acc Chem Res*, 2016, 49(1): 96–105.
- [6] 郭建业, 陈智武, 苏力军, 等. 辐射传热对二氧化硅气凝胶复合材料隔热性能的影响[J]. *硅酸盐学报*, 2023, 51(7): 1811–1818. GUO Jianye, CHEN Zhiwu, SU Lijun, et al. *J Chin Ceram Soc*, 2023, 51(7): 1811–1818.
- [7] SUZUKI Y, BERGER M H, D'ELIA D, et al. Synthesis and microstructure of a novel TiO_2 aerogel– TiO_2 nanowire composite[J]. *Nano*, 2008, 3(5): 373–379.
- [8] LIU F Q, JIANG Y G, PENG F, et al. Fiber-reinforced alumina–carbon core–shell aerogel composite with heat-induced gradient structure for thermal protection up to 1 800 °C[J]. *Chem Eng J*, 2023, 461: 141721.
- [9] PENG F, JIANG Y G, FENG J, et al. Thermally insulating, fiber-reinforced alumina–silica aerogel composites with ultra-low shrinkage up to 1 500 °C[J]. *Chem Eng J*, 2021, 411: 128402.
- [10] LI J X, AHMAD Z, CHEN J J, et al. Fabrication of SiC nanofiber aerogel felt with high-temperature thermal insulation performance[J]. *J Eur Ceram Soc*, 2024, 44(4): 1923–1931.
- [11] LI G Y, CHAI Y S, ZHANG X T. Laser ablation-induced boron nitride aerogels with intrinsic photoluminescence for efficient information encryption[J]. *Adv Funct Materials*, 2024, 34(23): 2314724.
- [12] LUO Y, LI K, CHEN Y T, et al. Single-atom and hierarchical-pore aerogel confinement strategy for low-platinum fuel cells[J]. *Adv Mater*, 2023, 35(31): e2300624.
- [13] LUO Y, YU L F, MEN J, et al. Ultralow thermal conductivity of single-atom doped carbon aerogel synthesized with a facile ambient-pressure-drying strategy[J]. *Carbon*, 2023, 213: 118167.
- [14] MEN J, FENG J Z, JIANG Y G, et al. Synthesis of environmentally friendly nanoporous monolithic carbon aerogels *via* ambient pressure drying for high-temperature thermal insulators[J]. *ACS Appl Nano Mater*, 2024, 7(7): 7132–7141.
- [15] 门静, 冯军宗, 姜勇刚, 等. 炭气凝胶的溶胶–凝胶合成工艺及其相关结构研究进展[J]. *硅酸盐学报*, 2024, 52(8): 2709–2721. MEN Jing, FENG Junzong, JIANG Yonggang, et al. *J Chin Ceram Soc*, 2024, 52(8): 2709–2721.
- [16] WU X D, LI W, SHAO G F, et al. Investigation on textural and structural evolution of the novel crack-free equimolar Al_2O_3 – SiO_2 – TiO_2 ternary aerogel during thermal treatment[J]. *Ceram Int*, 2017, 43(5): 4188–4196.
- [17] YAO N, CAO S L, YEUNG K L. Mesoporous TiO_2 – SiO_2 aerogels with hierarchical pore structures[J]. *Microporous Mesoporous Mater*, 2009, 117(3): 570–579.
- [18] QIN Y Y, PENG Q Y, DING Y J, et al. Lightweight, superelastic, and mechanically flexible graphene/polyimide nanocomposite foam for strain sensor application[J]. *ACS Nano*, 2015, 9(9): 8933–8941.
- [19] GU X H, ZHU S W, LIU S W, et al. Study of aerogel-modified recycled polyurethane nanocomposites[J]. *Nanomaterials*, 2023, 13(18): 2583.
- [20] CHEN Y M, ZHANG L, YANG Y, et al. Recent progress on nanocellulose aerogels: Preparation, modification, composite fabrication, applications[J]. *Adv Mater*, 2021, 33(11): e2005569.
- [21] SHIMIZU T, KANAMORI K, NAKANISHI K. Silicone-based organic–inorganic hybrid aerogels and xerogels[J]. *Chemistry*, 2017, 23(22): 5176–5187.
- [22] URATA S, KUO A T, MUROFUSHI H. Origin of flexibility of organic–inorganic aerogels: Insights from atomistic simulations[J]. *J Phys Chem C*, 2018, 122(35): 20555–20563.
- [23] WANG L K, FENG J Z, JIANG Y G, et al. Thermal conductivity of polyvinylpolymethylsiloxane aerogels with high specific surface area[J]. *RSC Adv*, 2019, 9(14): 7833–7841.
- [24] ZHOU X P, WANG Y F, XIAO L J, et al. Preparing carbon black

- aerogel quickly by chemical vapor deposition[J]. *Compos Commun*, 2023, 37: 101460.
- [25] SONG L M, FAN B B, CHEN Y Q, et al. Multifunctional SiC nanofiber aerogel with superior electromagnetic wave absorption[J]. *Ceram Int*, 2022, 48(17): 25140–25150.
- [26] SONG L M, ZHANG F, CHEN Y Q, et al. Multifunctional SiC@SiO₂ nanofiber aerogel with ultrabroadband electromagnetic wave absorption[J]. *Nanomicro Lett*, 2022, 14(1): 152.
- [27] SU L, WANG H J, NIU M, et al. Ultralight, recoverable, and high-temperature-resistant SiC nanowire aerogel[J]. *ACS Nano*, 2018, 12(4): 3103–3111.
- [28] XU X, ZHANG Q Q, HAO M L, et al. Double-negative-index ceramic aerogels for thermal superinsulation[J]. *Science*, 2019, 363(6428): 723–727.
- [29] BI H, CHEN I W, LIN T Q, et al. A new tubular graphene form of a tetrahedrally connected cellular structure[J]. *Adv Mater*, 2015, 27(39): 5943–5949.
- [30] BI H, LIN T Q, XU F, et al. New graphene form of nanoporous monolith for excellent energy storage[J]. *Nano Lett*, 2016, 16(1): 349–354.
- [31] SONG L M, WU C W, ZHI Q, et al. Multifunctional SiC aerogel reinforced with nanofibers and nanowires for high-efficiency electromagnetic wave absorption[J]. *Chem Eng J*, 2023, 467: 143518.
- [32] MIKHALCHAN A, FAN Z, TRAN T Q, et al. Continuous and scalable fabrication and multifunctional properties of carbon nanotube aerogels from the floating catalyst method[J]. *Carbon*, 2016, 102: 409–418.
- [33] ACAUAN L H, KAISER A L, WARDLE B L. Direct synthesis of carbon nanomaterials via surface activation of bulk copper[J]. *Carbon*, 2021, 177: 1–10.
- [34] SEHRAWAT M, RANI M, SHARMA S, et al. Floating catalyst chemical vapour deposition (FCCVD) for direct spinning of CNT aerogel: A review[J]. *Carbon*, 2024, 219: 118747.
- [35] WANG Z, HOU Y C, HAO H Q, et al. Scalable preparation of SiC@SiO₂ nanocable aerogels for broadband microwave absorption using low-cost carbon source[J]. *Carbon*, 2023, 211: 118092.
- [36] WANG Z, LIU J X, HAO H Q, et al. Microwave absorption enhancement by SiC nanowire aerogels through heat treatment-based oxidation modulation[J]. *Carbon*, 2024, 217: 118622.
- [37] ABDULLAH H B, IRMAWATI R, ISMAIL I, et al. Utilization of waste engine oil for carbon nanotube aerogel production using floating catalyst chemical vapor deposition[J]. *J Clean Prod*, 2020, 261: 121188.
- [38] ALEXANDER R, KAUSHAL A, PRAKASH J, et al. Porosity control of CNT aerogel and its conversion to CNT fiber in floating catalyst chemical vapour deposition[J]. *J Porous Mater*, 2023, 30(2): 507–520.
- [39] ALEXANDER R, KHAUSAL A, BAHADUR J, et al. Bi-directional catalyst injection in floating catalyst chemical vapor deposition for enhanced carbon nanotube fiber yield[J]. *Carbon Trends*, 2022, 9: 100211.
- [40] HOECKER C, SMAIL F, PICK M, et al. The influence of carbon source and catalyst nanoparticles on CVD synthesis of CNT aerogel[J]. *Chem Eng J*, 2017, 314: 388–395.
- [41] HOECKER C, SMAIL F, PICK M, et al. The dependence of CNT aerogel synthesis on sulfur-driven catalyst nucleation processes and a critical catalyst particle mass concentration[J]. *Sci Rep*, 2017, 7(1): 14519.
- [42] MOON S Y, KIM B R, PARK C W, et al. Hicrystallinity single-walled carbon nanotube aerogel growth: Understanding the real-time catalytic decomposition reaction through floating catalyst chemical vapor deposition[J]. *Chem Eng J Adv*, 2022, 10: 100261.
- [43] CHENG G M, CHANG T H, QIN Q Q, et al. Mechanical properties of silicon carbide nanowires: Effect of size-dependent defect density[J]. *Nano Lett*, 2014, 14(2): 754–758.
- [44] ZEKENTES K, ROGDAKIS K. SiC nanowires: Material and devices[J]. *J Phys D: Appl Phys*, 2011, 44(13): 133001.
- [45] LU D, SU L, WANG H J, et al. Scalable fabrication of resilient SiC nanowires aerogels with exceptional high-temperature stability[J]. *ACS Appl Mater Interfaces*, 2019, 11(48): 45338–45344.
- [46] TAN R X, FAN Z Q, XIE Z Y, et al. Fabrication of large-sized high density bulk isotropic pyrocarbon materials of a special composite microstructure by fixed-bed chemical vapor deposition[J]. *Carbon*, 2016, 101: 439–448.
- [47] YIN T, JIANG B Y, SU Z A, et al. Numerical simulation of carrier gas effects on flow field, species concentration and deposition rate in the chemical vapor deposition of carbon[J]. *N Carbon Mater*, 2018, 33(4): 357–363.
- [48] YU S J, CHEN Z F, WANG Y, et al. Preparation and thermal insulation analysis of SiC_w-SiC foam with hollow skeletons via carbon foam template CVI method[J]. *Mater Charact*, 2017, 134: 296–301.
- [49] LI Y L, KINLOCH I A, WINDLE A H. Direct spinning of carbon nanotube fibers from chemical vapor deposition synthesis[J]. *Science*, 2004, 304(5668): 276–278.
- [50] HOECKER C, SMAIL F, BAJADA M, et al. Catalyst nanoparticle growth dynamics and their influence on product morphology in a CVD process for continuous carbon nanotube synthesis[J]. *Carbon*, 2016, 96: 116–124.
- [51] STALLARD J C, TAN W, SMAIL F R, et al. The mechanical and electrical properties of direct-spun carbon nanotube mats[J]. *Extreme Mech Lett*, 2018, 21: 65–75.
- [52] HAN W Q, BRUTCHEY R, TILLEY T D, et al. Activated boron nitride derived from activated carbon[J]. *Nano Lett*, 2004, 4(1): 173–176.
- [53] ROUSSEAS M, GOLDSTEIN A P, MICKELSON W, et al. Synthesis of highly crystalline sp²-bonded boron nitride aerogels[J]. *ACS Nano*, 2013, 7(10): 8540–8546.
- [54] SONG Y X, LI B, YANG S W, et al. Ultralight boron nitride aerogels via template-assisted chemical vapor deposition[J]. *Sci Rep*, 2015, 5: 10337.
- [55] KUTTY R G, SREEJITH S, KONG X H, et al. A topologically substituted boron nitride hybrid aerogel for highly selective CO₂ uptake[J]. *Nano Res*, 2018, 11(12): 6325–6335.
- [56] LI B B, YUAN X S, GAO Y, et al. A novel SiC nanowire aerogel consisted of ultra long SiC nanowires[J]. *Mater Res Express*, 2019, 6(4): 045030.
- [57] SONG L M, CHEN Y Q, GAO Q C, et al. Low weight, low thermal conductivity, and highly efficient electromagnetic wave absorption of three-dimensional graphene/SiC-nanosheets aerogel[J]. *Compos Part A Appl Sci Manuf*, 2022, 158: 106980.
- [58] ZHANG Q Q, XU X, LIN D, et al. Hyperbolically patterned 3D graphene metamaterial with negative poisson's ratio and superelasticity[J]. *Adv Mater*, 2016, 28(11): 2229–2237.

Research Progress on Aerogels Prepared by Chemical Vapor Deposition

ZHAO Kongli, SUN Zhengyang, FENG Junzong, JIANG Yonggang, LI Liangjun, HU Yijie, FENG Jian

(Science and Technology on Advanced Ceramic Fibers and Composites Laboratory, College of Aerospace Science and Engineering, National University of Defense Technology, Changsha 410073, China)

Extended Abstract

Aerogel is a kind of highly dispersed solid material with extremely low density, in which nano-scale particles aggregate to form a nanoporous network structure with a gaseous dispersed medium in the voids. This material has some superior characteristics such as high specific surface area and low thermal conductivity, having broad application prospects in aerospace, building insulation, energy, environmental protection and other fields.

However, gelation process as a conventional preparation process of aerogel is mostly carried out in a liquid phase. The complex solvent replacement or sophisticated supercritical drying equipment is needed to avoid the influence of surface tension in the gel drying process, resulting in harsh preparation conditions, high cost, and cumbersome preparation process, and restricting the large-scale application of the aerogel in a certain extent.

The direct construction of aerogel nanoskeleton in vapor phase environment by chemical vapor deposition process can avoid the drying stage, which can greatly simplify the process and reduce its cost. Also, the aerogel prepared by chemical vapor deposition process has good mechanical properties, and the vapor phase process is suitable for the preparation of some aerogels with a special structure. This review represents the latest research progress on the chemical vapor deposition processes for preparation of aerogels (*i.e.*, template-less chemical vapor deposition and template-assisted chemical vapor deposition). In addition, the future research direction is also prospected.

Summary and Prospects This review summarizes recent research progress on the preparation of aerogels by chemical vapor deposition. The template-free chemical vapor deposition (CVD) method of the aerogel preparation can produce carbon material aerogels and multifunctional silicon carbide nanowire aerogels with superior performances for several hours. The template-assisted CVD method can customize the microstructure of the aerogel according to the template in order to achieve some special functions (*i.e.*, superelasticity, negative Poisson's ratio, *etc.*). The chemical vapor deposition process for the preparation of aerogel can completely avoid the influence of surface tension during the drying process and the preparation process is more efficient due to the absence of liquid phase, compared with the traditional aerogel liquid-phase preparation process. The existing research in the related field is not sufficient due to the presence of some problems. Some possible aspects of subsequent research include:

1) To further simplify the process. The template-assisted chemical vapor deposition method in the chemical vapor deposition preparation process for aerogels usually requires the specialized preparation of templates with aerogel structures, which increases the complexity of the process and is not conducive to large-scale production. Industrially produced fumed silica or fumed alumina has a structure similar to that of an aerogel, and the use of fumed silica or fumed alumina as a template to grow the desired material on its nano-skeleton is expected to reduce the cost of preparation of partial oxide aerogels.

2) To develop a chemical vapor deposition preparation process for aerogels with milder conditions. At present, the reaction temperature is mostly more than 1 000 °C when using chemical vapor deposition to prepare aerogels. The reaction conditions become milder and the requirements of equipment reduce through the introduction of catalysts and other methods, which is an important research aspect for the future development of chemical vapor deposition process of aerogel.

3) To broaden the scope of application of the material type of aerogel chemical vapor deposition process. From the existing reports, the chemical vapor deposition process can be used for the preparation of some aerogel types (*i.e.*, mainly carbon materials, carbides, borides and other aerogels). The reaction mechanism of the aerogel chemical vapor deposition preparation process needs to be further investigated. The chemical vapor deposition process can be used to prepare oxide aerogels (*i.e.*, silica and alumina) *via* utilizing the advantages of the chemical vapor deposition process (*i.e.*, short cycle time and no drying).

Keywords aerogel; chemical vapor deposition; template method; preparation process