

中国溶胶-凝胶历程回顾及进展

杨 辉^{1,2,4}, 李 跃^{1,4}, 朱满康³, 陈 露¹

(1. 浙江大学材料科学与工程学院, 杭州 310058; 2. 浙江大学浙江加州国际纳米技术研究院, 杭州 310058;
3. 北京工业大学材料科学与工程学院, 北京 100124; 4. 浙江大学温州研究院, 浙江 温州 325006)

摘 要: 溶胶-凝胶技术作为一种先进的材料合成技术已被广泛应用于粉体、薄膜、块体、多孔材料等不同类型的材料的制备中, 由此获得的材料相比传统方法得到的材料展现出更为优异的特征与性能。在过去的 20 年中, 中国在溶胶-凝胶技术的研究和应用领域也取得了长足的发展。为此, 本文总结回顾了我国溶胶-凝胶技术的发展历程, 并梳理了近 5 年来中国科研工作者在该领域所取得的研究成果。可以明显看到, 中国无论在溶胶-凝胶技术的学术领域还是产业应用领域都取得了长足的发展, 并将溶胶-凝胶技术带入了一个新的蓬勃发展阶段。

关键词: 溶胶-凝胶; 中国; 历程回顾; 纳米材料

中图分类号: TQ427.26 文献标志码: A 文章编号: 0454-5648(2024)08-2695-14

网络出版时间: 2024-05-17



溶胶-凝胶技术是材料学和化学相结合的交叉学科, 是以高化学活性化合物为前驱体, 通过水解、聚合、凝胶化等反应或过程, 再辅以特定的干燥、热处理等工艺或条件制备固体材料的方法^[1-4]。溶胶-凝胶法作为一种重要的湿化学制备方法被广泛应用于零维到三维纳米材料、块体材料、薄膜涂层材料、纤维材料等的制备中^[5-6]。溶胶-凝胶过程通过水解和缩聚反应, 将金属醇盐或其混合物组成的前驱体转变为特征尺度在 1 nm 至 1 μ m 的胶体分散液, 称之为“溶胶”, 并进一步反应生成具有网络结构的“凝胶”, 再通过相应的后处理步骤获得固态氧化物或其他化合物材料。大多数溶胶-凝胶过程都在低温下进行, 反应温度相比传统方法更低, 制备得到的材料在化学均匀性、掺杂均匀性、产物纯度方面具有与生俱来的优势, 并可通过前期制备过程的设计实现多组分、多物相材料的合成。

溶胶-凝胶技术的发展历程最早可追溯至 19 世纪中叶, 以 Ebelman 和 Braham 为代表的研究者发现, 将正硅酸乙酯(TEOS)在酸性条件下水解, 可以获得具有玻璃形态的二氧化硅材料^[2]。进入 20 世纪

后, 采用凝胶制备固态材料的方法开始受到更多研究者的关注。20 世纪 30 年代, Kistler 等^[7-8]采用水玻璃作为硅源, 结合甲醇超临界干燥工艺, 制备得到了气凝胶材料, 这也可视作首个重要的溶胶-凝胶产物。20 世纪 50 年代至 60 年代, Roy 等^[9]发现, 利用溶胶-凝胶法, 可获得具有极高化学均一度的凝胶, 并合成得到了包括 Al, Si, Ti, Zr 在内的多种新型陶瓷氧化物组分。1968 年, 美国杜邦公司 Stöber 开发出了高效制备胶体二氧化硅分散液的溶胶-凝胶技术, 合成了结构明确、均一度高的球形二氧化硅, 开发出 Ludox 胶体产品, 其对应的制备方法即为后来广为人知的 Stöber 法^[10]。1971 年, 德国 Schott 玻璃公司 Dislich 等^[11]发表了题为《多组分氧化物玻璃新方法》的论文, 采用含有钠、硼、铝、硅均相液体制备得到的胶体粉体, 在低至 630 $^{\circ}$ C 的热压条件下制造出派莱克斯型玻璃(Pyrex glass), 在玻璃研究领域引起了广泛的关注。此后, 越来越多的研究者开始关注溶胶-凝胶技术, 并提出了多种用于制备粉体、薄膜、块体、多孔材料等的方法, 应用于电子器件、催化、能源、金属腐蚀防护、光学等多个领域^[12-14]。

收稿日期: 2024-01-31。 修订日期: 2024-03-06。

基金项目: 广西科技重大专项(桂科 AA23062002); 国家自然科学基金(52072010)。

第一作者: 杨 辉(1962—), 男, 硕士, 教授。

通信作者: 李 跃(1988—), 男, 博士, 助理研究员。

Received date: 2024-01-31. Revised date: 2024-03-06.

First author: YANG Hui (1962—), male, Master, Professor.

E-mail: yanghui@zju.edu.cn

Correspondent author: LI Yue (1988—), male, Ph.D., Assistant Researcher.

E-mail: liyue8@zju.edu.cn

1 中国溶胶-凝胶学术组织发展历程

1981 年, 作为国际溶胶-凝胶大会前身的第一届国际凝胶玻璃及玻璃陶瓷研讨会在意大利北部城市帕多瓦举行, 标志着溶胶-凝胶技术发展进入快速发展的阶段^[15]。中国溶胶-凝胶研究也始于 20 世纪 80 年代, 最早研究单位有浙江大学、中国科学院上海硅酸盐研究所、中国科学院上海光机所、中国建材研究总院等^[16]。为了与国际溶胶-凝胶技术的最新研究保持同步, 1990 年, 首届“全国溶胶-凝胶科学与技术学术会议”在浙江大学邵逸夫科学馆召开, 来自全中国 20 多所大专院校、科研单位的 60 多名专家学者参加本次会议, 共收到交流学术论文 45 篇。这次活动及其后续的 2 次系列会议标志着中国

溶胶-凝胶时代的开端和快速发展。2006 年, “全国溶胶-凝胶科学与技术学术会议”正式更名为“中国溶胶-凝胶学术研讨会暨国际论坛”, 并于温州大学举行, 会议吸引了 160 余人参会。此后, 该会议每隔 2 至 3 年举办, 为中国溶胶-凝胶技术领域的学术交流提供了优质的平台。2008 年, 中国硅酸盐学会溶胶-凝胶分会成立, 理事长由浙江大学杨辉教授担任, 标志着中国溶胶-凝胶技术专业学会的正式成立。分会的成立团结和组织了中国从事溶胶-凝胶的研究人员, 促进了溶胶-凝胶的研究与产业发展, 为中国科技进步和经济发展做出了贡献。此外, 由分会主办的中国溶胶-凝胶青年学者论坛于 2015 年开始每隔 2 年定期举办, 为该领域青年学者提供了学术交流与合作的平台。



图 1 1990 年首届“全国溶胶-凝胶科学与技术学术会议”在浙江大学召开

Fig. 1 First national conference on sol-gel science and technology was held at Zhejiang University in 1990



图 2 中国硅酸盐学会溶胶-凝胶分会第一届理事会合照

Fig. 2 Group photo of the first council of the sol-gel committee of the Chinese Ceramic Society

中国硅酸盐学会溶胶-凝胶分会不仅积极举办中国国内的溶胶-凝胶学术交流活动,还致力于推动国际学术交流与发展。2011 年 8 月 28 日~9 月 2 日,第 16 届国际溶胶-凝胶大会在中国杭州成功举办,是中国首次承办溶胶-凝胶领域这一最具权威性的学术会议。此次会议受到了国际溶胶-凝胶学会的高度评价,国际溶胶-凝胶学报(*Journal of Sol-Gel Science and Technology*)主编 Michel Aegerter 教授后来提到,从此次会议中可以明显感受到,溶胶-凝胶技术的进步不仅局限于玻璃材料基础研究领域,同时向现代社会迫切需求的例如能源和生物技术等应用领域发展^[17]。日本大阪大学 Tsutomu Minami 教授也表示,此次会议为每位参会者提供了交换想法、拓展新的研究和合作领域的机会,同时也看到了学术界和产业界之间存在的紧密合作的需求^[17]。

2 溶胶-凝胶领域的学术研究进展

近 10 年(2014~2023 年),全球溶胶-凝胶领域相关论文呈稳步增长,总数达 128 627 篇(2023 年论文尚未完整收录),如图 3 所示。其中,由中国科研人员发表的溶胶-凝胶论文占全球的 32.5%(见图 4)。10 年间,中国发表的溶胶-凝胶论文每年占比保持在 23%以上,在全球处于领先地位,其中 2022 年占比更是达到了 50%。同时,全球溶胶-凝胶论文发表排名前十的机构中有 5 家来自于中国的科研院所,分别为中国科学院系统、中国科学院大学、四川大学、浙江大学和华南理工大学(见表 1)。

表 1 近 10 年(2013~2022 年)全球溶胶-凝胶论文发表排名前十的科研院所(根据 Web of Science 数据库统计,包含关键词 sol-gel, 统计时间 2024 年 1 月)

Table 1 Top 10 of universities and research institutes worldwide publishing in sol-gel field from 2014 to 2023 (statistics from Web of Science containing keyword “sol-gel”, January 2024)

Ranking	Research organizations	Number of publications
1	System of Chinese Academy of Sciences (CAS)	4 451
2	French National Research Center System (CNRS)	2 574
3	Indian Institute of Technology System (IIT)	2 062
4	Russian Academy of Sciences (RAS)	1 550
5	University of Chinese Academy of Sciences	1 420
6	Sichuan University	1 244
7	Islamic Azad University	1 179
8	Zhejiang University	1 146
9	The University of California System	948
10	South China University of Technology	946

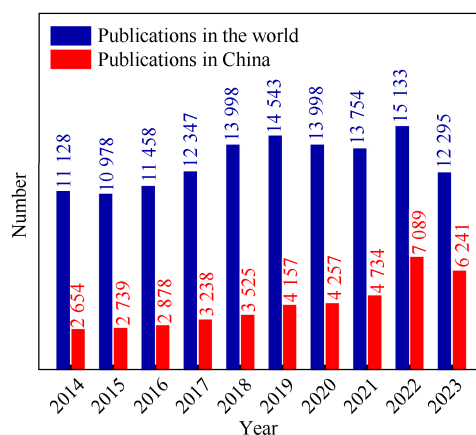


图 3 2014~2023 年全球和中国学者在溶胶-凝胶方面论文发表情况(根据 Web of Science 数据库统计,包含关键词 sol-gel, 统计时间 2024 年 1 月)

Fig. 3 Number of scientific papers worldwide from 2014 to 2023 (statistics from Web of Science based on the keyword “sol-gel”, January 2024)

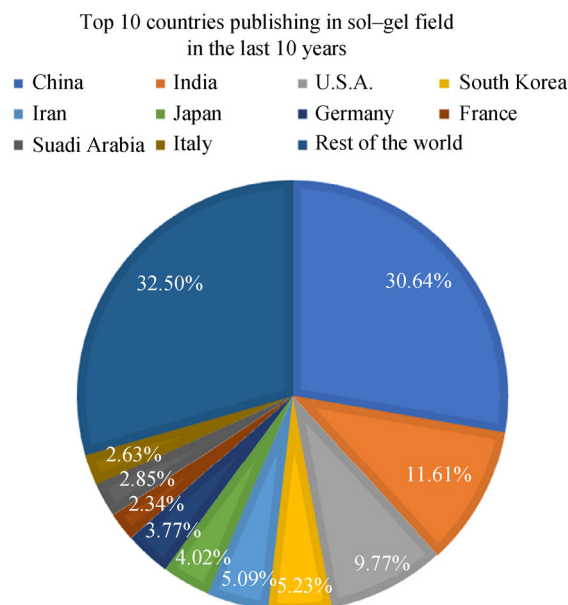


图 4 2014~2023 年溶胶-凝胶论文发表数排名前 10 的国家(根据 Web of Science 数据库统计,包含关键词 sol-gel, 统计时间 2024 年 1 月)

Fig. 4 Top 10 countries publishing in sol-gel field from 2014 to 2023 (statistics from Web of Science containing keyword “sol-gel”, January 2024)

中国科研机构及学者发表的溶胶-凝胶领域论文涵盖了溶胶-凝胶法制备纳米粉体、纤维、功能涂层、气凝胶、水凝胶等多种新型材料的方法,并将其应用于光学、电子、传感、催化、储能、药物、分离等众多领域^[18-26]。本文回顾并梳理了近年来中国科研机构及学者在溶胶-凝胶领域发表的代表性研究成果,这些研究成果通常采用溶胶-凝胶工艺制备具有新功能或更高性能的先进材料。由于篇幅所

限,本文难以详尽地涵盖所有中国溶胶-凝胶学术领域的重要成果,但透过对中国溶胶-凝胶学术领域最新发展和突破的概括性介绍,仍能窥见中国在此领域研究的全面性和重要意义。2023 年出版发行的由杨辉、朱满康、樊先平、罗仲宽等编写的《溶胶-凝胶前沿技术及应用》更为详实地论述了溶胶-凝胶领域的新成果、新应用和新趋势,为人们更深入地了解中国溶胶-凝胶研究的全面性和重要意义提供了重要参考。本书为国家出版基金项目“十四五”时期国家重点出版物,出版专项规划项目,“中国战略性新兴产业——前沿新材料”丛书之分册,主要内容包包括阶层多孔材料、气凝胶、氧化铝微球、介电材料、功能氧化物薄膜及有机凝胶材料等,突出溶胶-凝胶领域的前瞻性、创见性、科学性,以及学科间的交叉与渗透。

2.1 溶胶-凝胶法制备纳米粉体材料

纳米尺度下的材料因其与常规块体材料不同的优异物理和化学特性受到了广泛的关注。纳米粉体材料多采用水热法、溶剂热法、共沉淀法、溶胶-凝胶法等湿化学方法制备。其中,溶胶-凝胶法在制备均一粒径、特定形貌、可控成分的纳米粉体材料方面具有独特的优势^[27–29]。由于这些优点,溶胶-凝胶法制备的纳米粉体被广泛应用于电子陶瓷、微波介质、电工合金、储能、光催化等领域。

近年来,新能源领域的快速发展也推动了锂电池、钠电池电极、超级电容器、燃料电池等相关的储能材料的技术进步^[30–32]。为此,大量中国研究者开始将溶胶-凝胶技术应用在具有高能量密度、优异循环稳定性、高安全性的新型电极粉体材料的制备中^[33–38]。例如,南京理工大学夏晖课题组^[38]利用金属硫化物具有较高的钠离子电池比容量,针对金属硫化物存在的体积膨胀高、循环稳定性差、电极动力过程不理想等问题,采用溶胶-凝胶原位生长方式制备了 CoS_x 量子点修饰氮/硫掺杂的碳纳米片二维异质结结构(见图 5)。该方法无需进一步的硫化反应,且碳纳米片中掺杂的氮、硫元素可大幅提高电极材料的导电性能,并增加钠离子的储存点位。此异质结复合材料作为钠离子电池正极材料,具有优异的倍率性能及循环稳定性,采用该电极材料制备的电池在电流密度为 $0.2 \text{ A} \cdot \text{g}^{-1}$ 时的比容量可达 $414 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$ 。

在掺杂光催化粉体材料的制备方面,溶胶-凝胶法具有工艺简单、操作灵活、制备条件易于控制等优点,因此在光催化材料的研究和应用中得到了广泛的应用。利用掺杂过渡金属或稀有元素可以调节光催

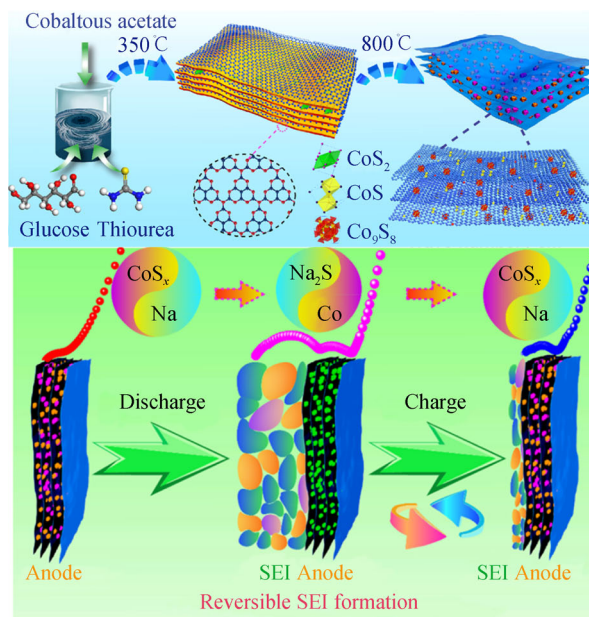


图5 $\text{CoS}_x\text{@NSC}$ 复合纳米粉体的制备过程和电极表面可逆 SEI 层形成过程示意图^[38]

Fig. 5 Schematic illustration of synthesis procedure for the $\text{CoS}_x\text{@NSC}$ nanocomposite and the reversible solid electrolyte interface (SEI) layer formation on the $\text{CoS}_x\text{@NSC}$ electrode^[38]

化材料的电子结构,从而创造出更多的催化反应活性中心或空穴捕获位点,提高电子-空穴对复合速率,提高光催化材料的催化效率^[39–43]。例如,中国矿业大学(北京)郑水林团队^[44]采用一种温和的溶胶-凝胶工艺,结合化学剥离和自组合法,制备得到了石墨相氮化碳/二氧化钛/高岭石三维异质结纳米复合材料(见图 6),并应用于可见光下对环丙沙星污染物的分解。该三明治结构赋予了其较好的光捕获及载流子分离及运输效率,使过氧自由基在分解反应中起到了更好的作用。所得复合材料对污染物的表观分解速率相比纯 TiO_2 、 $\text{g-C}_3\text{N}_4$ 与 P25 分别提高到了 5.35 倍、6.35 倍和 4.49 倍,且对于金黄色葡萄球菌具有更优异的杀菌能力。

在电磁屏蔽材料方面,通过溶胶-凝胶工艺对材料宏观组分和微观结构的调控,可改变微波吸附材料的自耗散和微波衰减能力,进而实现高效的电磁吸收性能^[45–47]。南京航空航天大学姬广斌团队^[45]采用溶胶-凝胶工艺制备出了掺杂不同 Fe 含量的钙钛矿 LaCoO_3 纳米粉体材料。结果表明, $\text{LaCo}_{0.9}\text{Fe}_{0.1}\text{O}_3$ 具有优异的微波吸收性能,在 1.95 mm 厚度时的最小反射损失在 -41 dB 左右,有效吸收带宽可达 5.16 GHz,并可有效覆盖 X 波段的吸收。另外, Wang 等^[47]采用溶胶-凝胶法,并结合牺牲模板技术制备了负载 Fe_3N 的二维多孔碳复合材

料(见图 7), 通过磁性/介电材料的组合及多孔结构的设计优化了材料的阻抗匹配特性, 从而增强了微

波吸收能力, 其有效带宽可达 6.76 GHz, 最小反射损失为-65.6 dB。

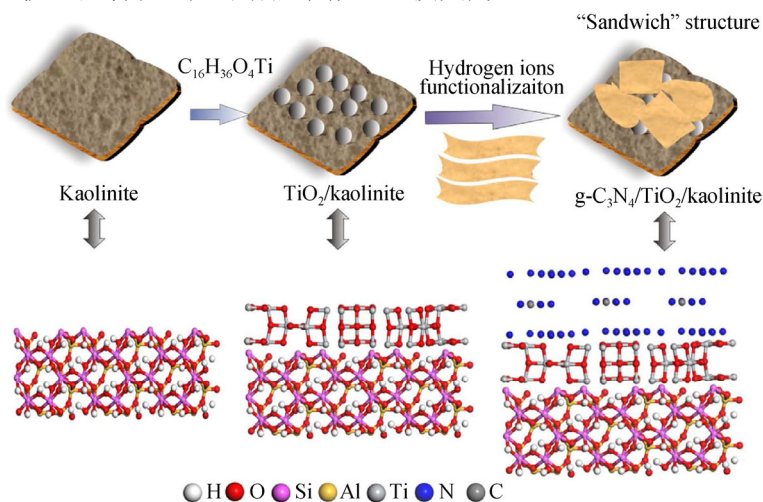
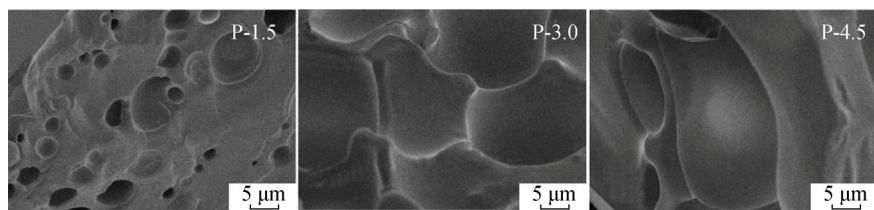


图 6 石墨相氮化碳/二氧化钛/高岭石三维异质结纳米复合光催化材料制备过程示意图^[44]

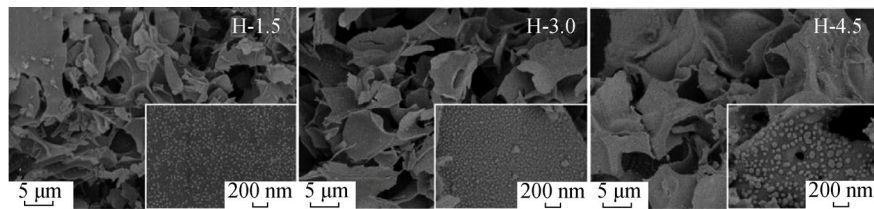
Fig. 6 Schematic illustration of synthesis process for g-C₃N₄/TiO₂/kaolinite photocatalytic nanocomposite^[44]



(a) SEM images of the gel-precursor

(c) SEM images of the gel-precursor

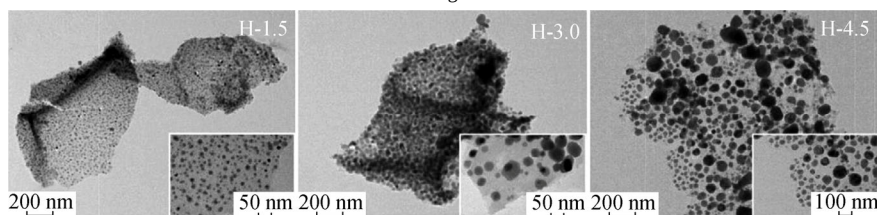
(e) SEM images of the gel-precursor



(b) SEM images of samples synthesized with different amounts of Fe(NO₃)₃·9H₂O after annealing: H-1.5

(d) SEM images of samples synthesized with different amounts of Fe(NO₃)₃·9H₂O after annealing: H-3

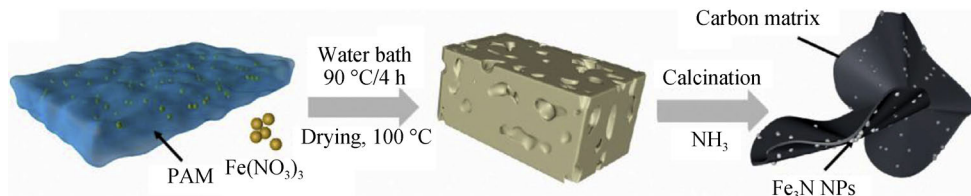
(f) SEM images of samples synthesized with different amounts of Fe(NO₃)₃·9H₂O after annealing: H-4.5



(g) TEM images of H-1.5

(h) TEM images of H-3

(i) TEM images of H-4.5



(j) Synthesis diagram of two-dimensional flaky Fe₃N alloy/carbon

图 7 二维片状 Fe₃N/多孔碳复合材料的 SEM 照片及制备过程^[45]

Fig. 7 SEM images and the synthesis diagram of two-dimensional flaky Fe₃N alloy/carbon^[45]

在导热粉体材料方面,西北工业大学顾军渭课题组采用溶胶-凝胶原位生长方法在氮化硼纳米片表面合成了碳化硅纳米颗粒,并作为导热和绝缘填料引入环氧涂层中(见图8)^[48]。该异质纳米结构可协同增强环氧复合材料的热传导性能,碳化硅纳米颗粒可作为相邻氮化硼纳米片之间的导热通道,提高

了复合材料的导热性能。在填料添加量在 20%(质量分数)时复合材料的导热系数(λ)为 $0.89 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$,是纯环氧涂层的 4.1 倍,相比直接添加氮化硼纳米片和碳化硅纳米颗粒的环氧复合材料提高了 70%,同时展现了较好的绝缘性、击穿强度、体积电阻率以及表面电阻率。

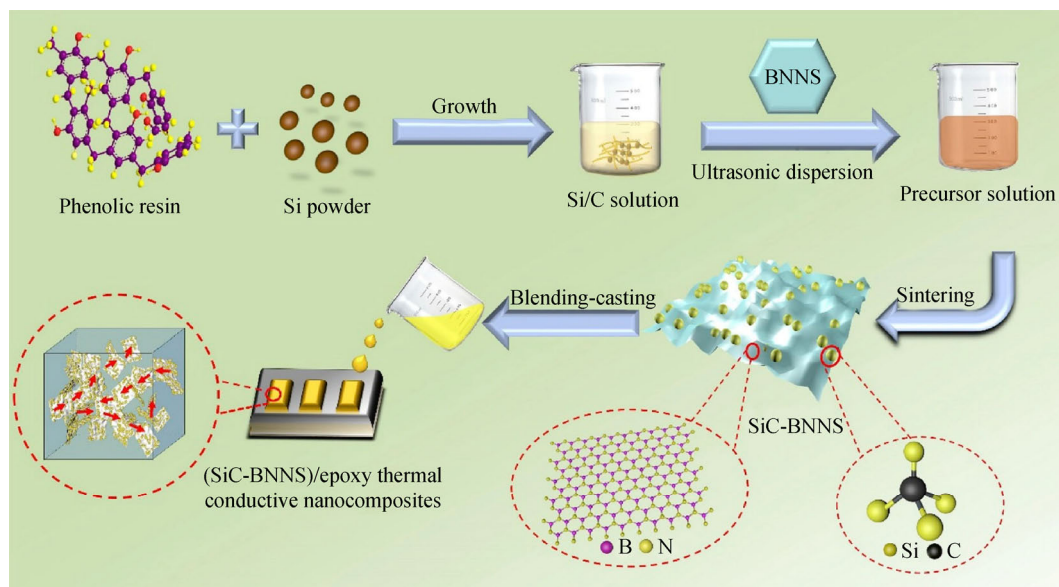


图8 SiC-BNNS 纳米填料及其环氧复合导热材料制备示意图^[48]

Fig. 8 Schematic illustration for the fabrication of hetero-structured SiC-BNNS fillers and (SiC-BNNS)/epoxy thermally conductive nanocomposites^[48]

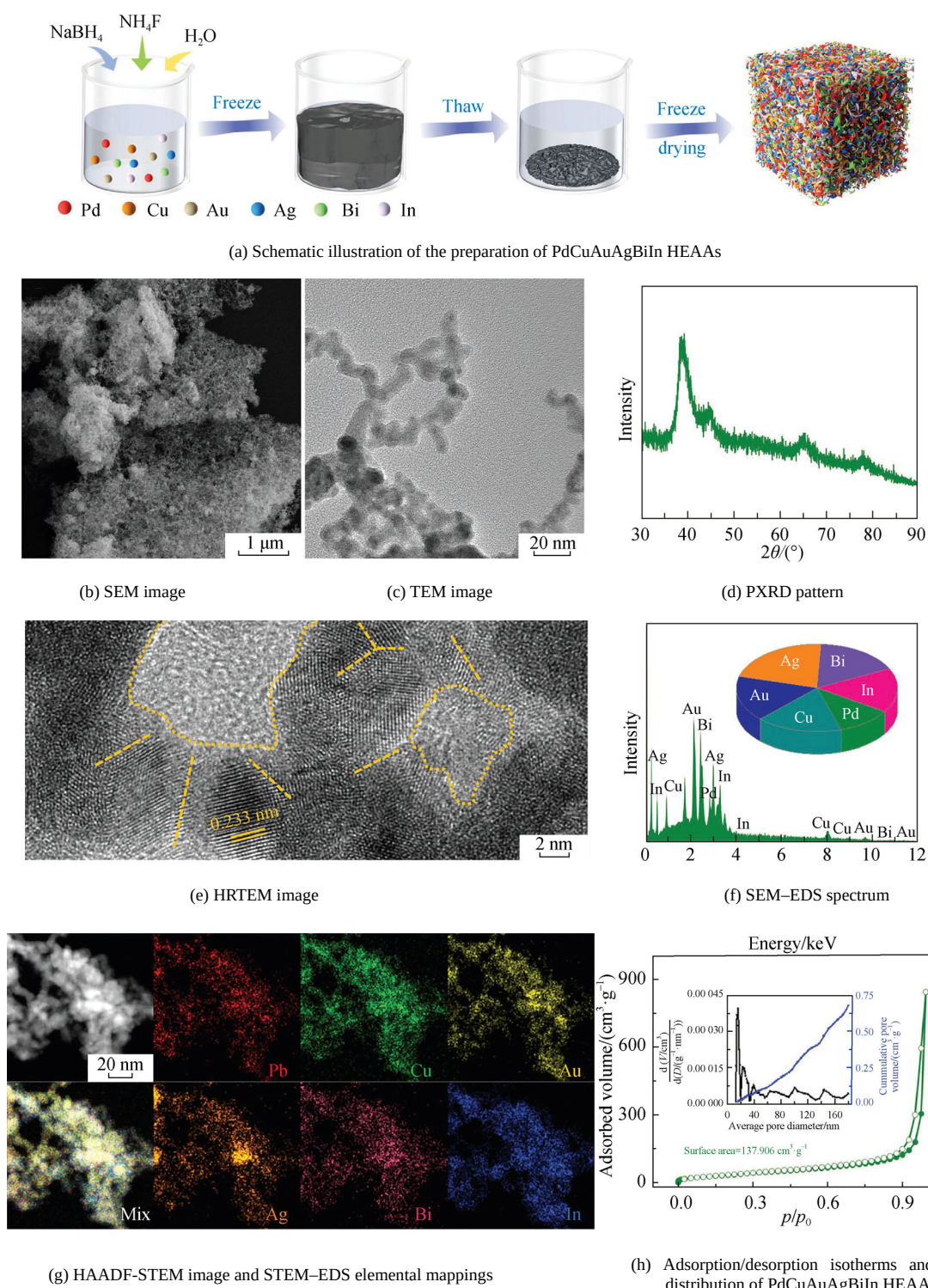
在二维片层结构纳米材料方面,浙江大学郭兴忠等^[49]采用络合辅助溶胶-凝胶法,以四水钼酸铵为钼源、硫代乙酰胺为硫源、三胺五乙酸为络合剂形成体凝胶,经过 $1\,000\text{ }^{\circ}\text{C}$ 烧结处理制备了 MoS_2 纳米片层,通过钼/硫比例调控的多层堆叠作用,形成了六方形晶体 MoS_2 纳米颗粒,结果表明,该 MoS_2 纳米片层具有作为锂电池负极材料的可能性。东北大学孟凡利团队^[50]采用溶胶-凝胶法成功制备了具有丰富表面氧空位缺陷(O_v)及多孔结构的磷掺杂钙钛矿型 $\text{LaFe}_{1-x}\text{P}_x\text{O}_{3-\delta}$ 纳米片。结果表明,磷掺杂能诱导产生 O_v 缺陷并调控材料的前沿电子轨道能级,从而提高了化学吸附氧含量以及表面氧化还原反应,使 $\text{LaFe}_{1-x}\text{P}_x\text{O}_{3-\delta}$ 纳米片展现出优异的丙酮探测传感性能,相比纯 LaFeO_3 气体传感器,其最佳操作温度降低到 $180\text{ }^{\circ}\text{C}$,响应值提高接近 2 倍,检测限达到 10^{-9} 级(50×10^{-9})。

2.2 溶胶-凝胶法制备块体材料

溶胶-凝胶法作为一种湿化学制备过程,可广泛

应用于玻璃、陶瓷、玻璃陶瓷、气凝胶、整体柱等块体及纤维材料的制备^[51–52]。

气凝胶作为溶胶-凝胶法制备的一种重要的多孔材料,其特有的三维网络纳米多孔结构使其具有超低密度、超低热导率、超高比表面积以及超强吸附能力等特性,这方面已有相关文献进行综述,本文不再对此进行叙述^[53–55]。自 1931 年被发现以来,气凝胶在储能、催化剂载体、传感、化学吸附、隔热、生物医药等领域受到广泛的关注^[14, 56]。而通过对高熵合金与气凝胶的结合获得的高熵合金气凝胶(HEAAs)同时具有二者的优点,成为近年来受到关注的催化反应新平台。Li 等^[57]采用冻融法制备了一系列高熵合金气凝胶(见图 9),利用 HEAAs 独特的三维网络结构、金属间的强相互作用以及表面丰富的不饱和位点,优化了催化剂表面 HCOO^* 中间体的吸附和解吸强度,将其作为 CO_2 还原反应的电催化剂呈现出高活性、高耐久性等优点,为二氧化碳减排开辟了新的路径。

图 9 PdCuAuAgBiIn HEAAs 制备过程及其微观特性表征^[57]Fig. 9 Schematic illustration of the preparation of PdCuAuAgBiIn HEAAs and corresponding microscopic characterization^[57]

在溶胶-凝胶法制备材料方面, 上海交通大学李良团队^[58]通过溶胶-凝胶工艺, 将 CsPbBr₃ 量子点引入氧化硅/氧化铝整体柱中, 得到了透明发光整体材料, 其荧光量子效率可达 90%, 强蓝光照射下的光稳定时间可达 300 h。溶胶-凝胶技术也是制备分级多孔块体材料的重要方法^[59]。Feng

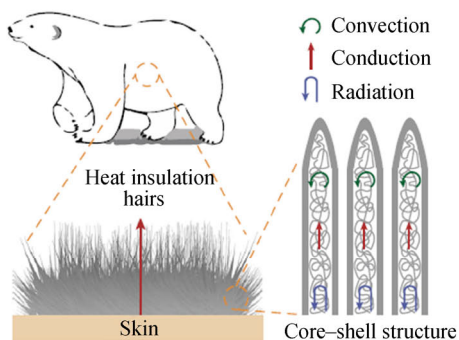
等^[60]采用溶胶-凝胶结合相分离法制备出了分级多孔 ZnFe₂O₄, 并在表面包覆了氮掺杂碳外层结构, 应用于锂电池正极材料。其具有的中空介孔骨架结构可有效改善电极与电解液之间的界面接触区域, 同时促进锂离子的传输速率, 表面包覆的氮掺杂碳层可增强多孔材料的电导率及机械强

度,在反复充放电过程中加速电子的迁移,使材料展现出了优异的可逆容量、比容量等锂电池储能特性^[60]。

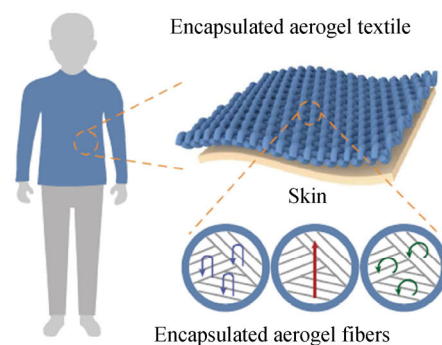
2.3 溶胶-凝胶法制备纤维材料

溶胶-凝胶法广泛应用于纤维材料的制备中^[61–64]。其中,气凝胶纤维因其优异的隔热性能,在纺织品领域具有广阔的前景,但气凝胶纤维的脆弱性导致其加工性能不理想,限制了进一步的发展^[65]。近期,浙江大学柏浩教授团队提出,通过模仿北极熊毛的

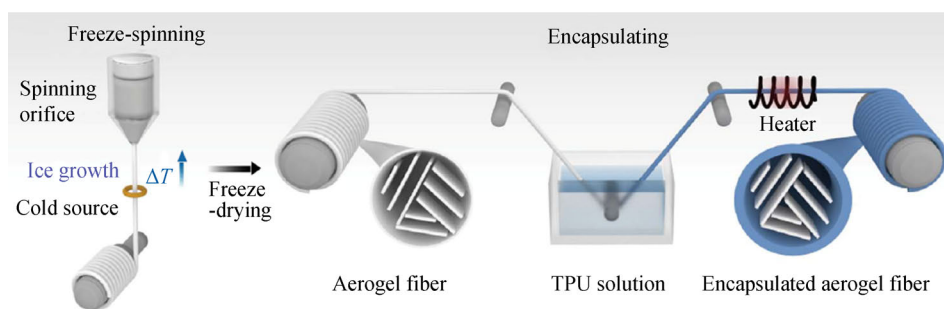
核-壳结构,在壳聚糖气凝胶纤维表面包覆一层可拉伸的热塑性聚氨酯壳层,获得了一种高分子壳层封装的气凝胶纤维(EAFs)(见图 10),纤维具有优异的力学性能(90%孔隙度时的拉伸形变可达 1 000%)以及远低于传统织物纤维的热导率 $[(26.9 \pm 1.8) \text{ mW} \cdot \text{m}^{-1} \cdot \text{K}^{-1}]$,并在 10^4 次循环拉伸后仍能保持稳定的隔热性能,且具有优异的耐洗性、染色性和柔韧性。在该气凝胶纤维织物厚度仅为羽绒厚度的 1/5 时,就可取得相近的隔热效果^[65–66]。



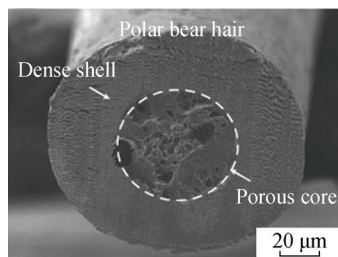
(a) Schematic illustration of thermal insulation principles of polar bear hairs



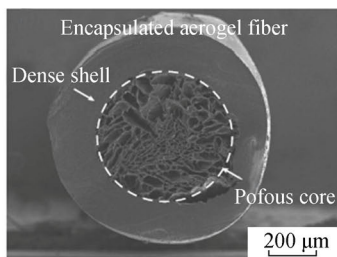
(b) Schematic illustration of thermal insulation principles of reported EAFs



(c) EAFs are prepared by freeze-spinning followed by a coating-drying step



(d) SEM images of polar bear hair



(e) SEM images of EAF



(f) Optical images of as-prepared fiber reels showing the potential of large-scale fabrication

图 10 模仿北极熊毛的核壳结构气凝胶纤维的设计及制备过程^[66]

Fig. 10 Design and fabrication of core-shell aerogel fiber mimicking polar bear hair^[66]

2.4 溶胶-凝胶法制备功能涂层

溶胶-凝胶作为一种湿化学合成方法在功能涂层的制备方面具有独特的优势,可用于合成无机涂层或有机-无机复合涂层,应用于金属防腐、防反射、

防雾、防污、增硬、增透、疏水等多种功能涂层应用领域中^[67]。相比气相沉积、电化学沉积等传统的表面处理方法,溶胶-凝胶工艺无需昂贵的设备或高温处理工艺,是一种低沉本、低污染制备高性能功

能涂层的方法。通过在溶胶-凝胶过程中引入有机组分可获得具有优异的涂层致密度、疏水性、硬度等特性的有机-无机复合防腐涂层, 大幅提高涂层对腐蚀介质的被动阻隔作用, 同时金属基材表面丰富的羟基能使其在固化过程中与涂层形成稳定的共价键合, 延缓腐蚀介质在涂层与金属基面间的渗透作用^[68]。通过对涂层组分配比以及制备工艺的调控或引入功能组分还可实现溶胶-凝胶涂层的超疏水、自清洁、自修复、防污、防冰冻等功能。

通过将封装有金属腐蚀抑制剂分子的纳米微胶囊引入到溶胶-凝胶防腐涂层中, 可实现涂层的自修复功能^[69-72]。浙江大学黄绎等采用溶胶-凝胶法, 在负载有金属缓蚀剂的 ZIF-8 复合 MOF 纳米结构表

面包覆介孔氧化硅壳, 获得了核/壳结构的缓释自修复纳米容器粉体材料, 可提高涂层腐蚀被动阻隔效应, 并实现涂层主动自修复功能, 协同提升溶胶-凝胶涂层的防腐蚀性能。另外, 溶胶-凝胶涂层还可应用于纺织品表面, 为织物提供多重的功能特性, 以实现阻燃、防蚊、防水、防油、抗菌、抗皱、防紫外线、自洁等功能^[73-74]。华南理工大学曾幸荣团队^[75]采用简便的一锅溶胶-凝胶法, 将经过氧等离子体活化的棉织物浸润在四乙氧基硅烷、羟基封端聚二甲基硅氧烷和聚磷酸铵的混合液中, 通过氢键作用在织物表面原位构筑了具有超疏水及阻燃功能的涂层(见图 11), 使织物具有优异的高疏水性、阻燃性、耐久性和自清洁能力。

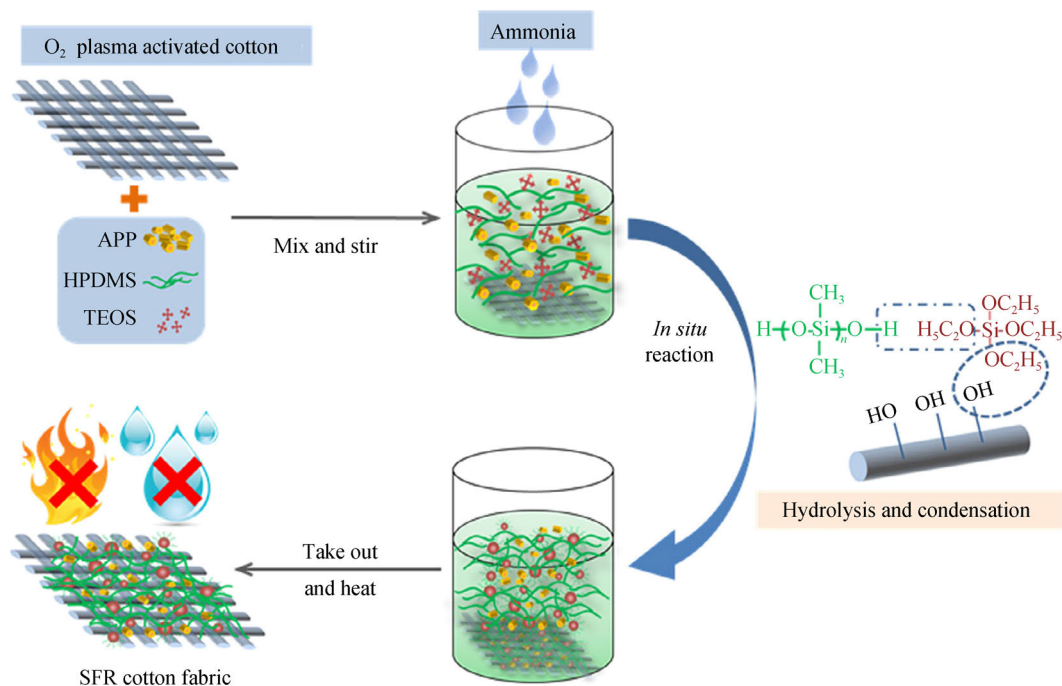


图 11 棉织物表面一锅法制备超疏水阻燃涂层过程图^[75]

Fig. 11 Schematic diagram of the one-pot fabrication process for superhydrophobic and flame-retardant coatings on cotton fabrics^[75]

3 溶胶-凝胶技术在产业界的应用

随着溶胶-凝胶技术的快速发展, 中国溶胶-凝胶学术成果也推动着其在产业界的发展, 溶胶-凝胶工艺开发的一系列新材料也进入了产业化应用阶段, 走入了人们的日常生活中。溶胶-凝胶法生产纳米氧化物及陶瓷粉体是溶胶-凝胶技术在中国产业界应用较为成熟的领域, 应用于半导体、光学部件抛光材料、功能涂层、高分子聚合物材料增强、催化载体材料等领域。相比传统机械研磨等“自上而下”的生产工艺, 溶胶-凝胶这一“自下而上”的制备方法生产的粉体具有纯度高、分散性好、稳定性好

等优点, 并可实现粉体颗粒理化特性的精准控制。浙江三时纪新材料科技有限公司采用溶胶-凝胶法, 实现了电子级球形二氧化硅封装材料的规模化生产, 与传统熔融法或爆燃法生产的微球相比, 具有粒度及其分布宽窄可控、掺杂均一性好、合成温度低等优势, 可满足高端芯片封装材料的性能需求。该产品突破了日本公司在这一领域的垄断, 被浙江省经济和信息化厅认定为 2022 年度浙江省首批次新材料(国际首批次)。

此外, 溶胶-凝胶技术也已广泛应用于功能涂层材料的生产中。据统计, 预计到 2027 年, 全球溶胶-凝胶功能涂层的市场规模将达到 48 亿美元, 其中,

中国市场的规模将达到 8.33 亿美元, 年复合增长率将达到 9.2%^[76]。浙江今飞摩轮有限公司联合浙江大学功能涂层团队研发的铝合金表面防腐一体化环保涂层材料, 满足了企业对铝合金表面环保型涂装的需求, 部分替代了原有电镀工艺, 减少了废水、重金属污染物、可挥发有机物的排放。杭州格灵新材料科技有限公司基于溶胶–凝胶渗透–硬化协同技术, 开发了建筑地坪用超硬耐磨纳米硬化涂层材料, 在传统硅酸盐地坪硬化的基础上进一步提高了地坪的硬度、寿命及防滑性能。上海宜瓷龙新材料科技有限公司基于溶胶–凝胶成膜原理开发了水性无机陶瓷涂料, 可用于铝合金、钢板、不锈钢板等金属基材的表面处理, 广泛应用于炊具、灶具、铝幕墙、建筑墙面等领域, 相比传统搪瓷板, 具有处理温度低、耐腐蚀性好、光泽度好等优点。在光学镀膜方面, 广西浦晶光学有限公司针对目前高端 PC(聚碳酸酯)光学镜片表面耐划伤性能差、透光率低、防雾功能缺乏、多涂层制备工艺复杂、生产成本高等产业技术瓶颈, 研发了基于溶胶–溶胶技术的防雾、耐磨、高透聚碳酸酯镜片制备技术, 并实现规模化生产, 推动高端 PC 光学镜片的功能化、多元化发展。

4 总结与展望

回顾和梳理溶胶–凝胶技术在中国的发展历程, 可以明显看到中国在这一领域取得的惊人成就和突破性进展。自溶胶–凝胶这一概念被提出以来, 溶胶–凝胶技术已经在多个领域展现出巨大的潜力, 从材料科学到生命科学, 再到环境工程。中国科研人员在这一过程中发挥了关键作用, 推动了该技术的不断演进。中国在溶胶–凝胶技术方面的成功经验不仅体现在科研领域, 还在工业制造和产业界得到了广泛应用。基于溶胶–凝胶技术开发的新型功能材料为各个行业带来了创新机会, 促进了科技与产业的融合, 也对中国经济的可持续发展起到了推动作用。随着科学技术的不断发展和创新, 溶胶–凝胶技术面临着更多的机遇与挑战。预期溶胶–凝胶技术在未来将会在一些重要的方向进一步发展:

在基础科学研究方面:

1) 先驱体的功能化设计和构建: 溶胶–凝胶过程中的先驱体设计和构建是实现多元化、多维结构化材料合成的关键。通过精心设计和控制先驱体的化学成分、结构以及表面性质, 可以实现对材料导电性、光学性质、力学性能等关键特性的精准调控, 为制备具有特定性能和应用潜力的复杂材料提供了

可能性。

2) 与功能化离子溶剂的结合: 将溶胶–凝胶技术与功能化离子溶剂结合使用, 可以进一步扩展其在材料合成中的应用。功能化离子溶剂具有较高的溶解度、较低的表面张力以及可调控的溶解性能, 可以提供更广泛的反应条件和更多样化的溶剂环境。这有助于扩大溶胶–凝胶技术在电化学、催化剂等领域的应用范围, 促进材料的多元化和结构的精细调控。

3) 微区反应区域的构建: 通过微乳浊液、3D 打印、微区电化学等手段营造微区反应条件, 可以在保障材料多元组成均匀的情况下制备所需的纳米结构材料。这种方法使得在材料合成过程中可以更加精细地控制反应条件, 实现对材料结构和性能的精确调控, 对于实现纳米结构的均匀性和一致性至关重要。

在产业技术应用方面:

1) 不同尺度的球状粉末的制备: 球状粉末具有较高的流动性和均匀性, 适用于 3D 打印、喷涂涂料、陶瓷制备、粉末冶金等领域。通过溶胶–凝胶技术, 可以实现对球状粉末尺度、形貌和组成的精确控制, 从而满足不同应用领域的需求。

2) 深紫外处理、溶剂热等非高温处理工艺: 深紫外处理、溶剂热处理等方法可以避免高温处理对材料结构和性能的影响, 从而获得非晶态或晶态产物的凝胶薄膜或粉末, 对于一些特殊材料的制备具有重要意义, 同时也有助于节能减排和降低生产成本。

3) 气凝胶/水凝胶: 目前市场但对于耐高温气凝胶和非氧化物水凝胶存在较大的需求, 未来的发展方向之一是优化溶胶–凝胶工艺, 探索新的材料体系和处理方法, 以满足市场对高性能、多功能多孔材料的需求。

展望未来, 溶胶–凝胶技术在中国具有广阔的发展潜力, 我们期待溶胶–凝胶技术在更多领域得到广泛应用, 特别是在解决能源、环境和健康等重大问题上发挥更为重要的作用, 在未来继续为人类福祉和科技进步做出更为卓越的贡献。

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Retrospective Overview of Sol-Gel History in China and Recent Progress

YANG Hui^{1,2,4}, LI Yue^{1,4}, ZHU Mankang³, CHEN Lu¹

(1. School of Materials Science and Engineering, Zhejiang University, Hangzhou 310058, China;

2. Zhejiang-California Nano-Systems Institute, Zhejiang University, Hangzhou 310058, China;

3. College of Materials Science and Engineering, Beijing University of Technology, Beijing 100124, China;

4. Institute of Wenzhou, Zhejiang University, Wenzhou 325006, Zhejiang, China)

Extended Abstract

The sol-gel technology is an interdisciplinary field combining materials science and chemistry. It utilizes highly active chemicals as precursors, taking part in chemical reactions and treatment such as hydrolysis, polymerization, gelation, etc.. Solid product are often achieved by specific drying, heat treatment, or other processes/conditions. As an advanced wet-chemical preparation method, sol-gel technology finds widespread applications in the fabrication of zero-dimensional to three-dimensional nanomaterials, bulk materials, thin film coatings, fiber materials, etc. Materials obtained through this method exhibit superior characteristics and properties compared to those obtained through traditional methods. Most sol-gel processes are conducted at low temperatures, resulting in lower reaction temperatures compared to traditional methods. Materials prepared using this method possess inherent advantages in terms of chemical homogeneity, doping uniformity, and product purity. Moreover, the design of the early-stage preparation process enables the synthesis of multi-component materials with multi-phase.

Over the past two decades, China has made great progress in the research and application of sol-gel technology. Scientists have developed a wide range of methods for preparing novel materials using sol-gel techniques. These materials have been applied across various domains including optics, electronics, sensing, catalysis, energy storage, pharmaceuticals, separation, and many others. These achievements typically involve the preparation of advanced materials with novel functionalities or enhanced performance using sol-gel processes. Through this overview of the latest developments in the sol-gel academic field, one can appreciate the comprehensive research and significant contributions made in China.

The development of sol-gel technology can be traced back to the mid-19th century. As the 20th century progressed, the method of using gelation to prepare solid materials began to receive increased attention from researchers. More and more scholars began to focus on sol-gel technology, proposing various methods for preparing materials in various forms. These methods have found applications in multiple domains such as electronic devices, catalysis, energy, metal corrosion protection, optics, and others. In 1981, the First International Workshop on Glasses and Glass Ceramics from Gels was held in Padova, Italy, marking the rapid development phase of sol-gel technology. Sol-gel research in China also began in the 1980s, when many research institutions started extensively to work on sol-gel technology during this period. In 1990, the inaugural "National Conference on Sol-Gel Science and Technology" was held at Zhejiang University, marking the beginning of the sol-gel era in China. Subsequently, this conference has been held every 2 to 3 years, providing a high-quality platform for academic exchange in the field of sol-gel technology in China. In 2008, the Sol-gel Committee of the Chinese Ceramic Society was established, signifying the formal establishment of a professional association for sol-gel technology in China. The Sol-gel Committee of the Chinese Ceramic Society not only actively organizes academic activities within China but strives to promote communication with the abroad academic society and to organize international conferences as well. From August 28 to September 2, 2011, the 16th International Sol-gel Conference was held in Hangzhou, China. This marked the first time that China hosted this prestigious academic conference in the sol-gel field, receiving high praise from the international sol-gel community.

In recent years, Chinese research institutions and scholars have published an avalanche of papers in the field of sol-gel. Over the past decade (2014–2023), there has been a steady increase in global publications related to the sol-gel field, with a total of 128 627 papers. Among these, articles authored by Chinese researchers accounted for 32.5% of the global output, with this proportion reaching 50% in the year 2022. This paper focuses on highlighting some research achievements in the preparation of nano-powder materials, fiber materials, and functional coatings using the sol-gel method. It also discusses the application in energy storage, catalysis, electromagnetic shielding, thermal conductivity, luminescence, and thermal insulation.

With the rapid development of sol-gel technology, the achievements of the Chinese sol-gel academic community have also propelled its industrial development. Many new materials developed through sol-gel processes have entered the industrial application stage and become part of people's daily lives. The mass production of nano oxides and ceramic powders using the sol-gel method is well developed in China. It is applied in various fields such as semiconductors, optical component polishing materials, functional coatings, reinforcement of polymer materials, and catalytic carrier materials. Sol-gel technology has also been widely applied in the production of functional coating materials, used in applications such as anti-corrosion coatings for metals, optical coatings, and more.

Summary and prospects Since the concept of sol-gel was proposed, sol-gel technology has demonstrated tremendous potential in various fields, ranging from materials science to life sciences and environmental engineering. It is evident that China has made remarkable progress in both academic and industrial application of sol-gel technology, bringing it into a new stage of vigorous development. By reviewing and summarizing the development of sol-gel technology in China, one can clearly see the remarkable achievements and groundbreaking progress made in this field. Chinese researchers have played a key role in this process, driving the

continuous evolution of this technology. China's successful experiences in sol–gel technology are not only evident in scientific research but also widely applied in industrial manufacturing and sectors. Looking ahead, sol–gel technology is expected to focus on several key development directions in the future. In fundamental research, the study of sol–gel technology can focus on the functional design and construction of precursors, their combination with functionalized ionic solvents, and the construction of micro-reactive zones. In terms of industrial technology, sol–gel technology shows promising prospects in the preparation of spherical powders at different scales, deep ultraviolet treatment, non-high-temperature treatment processes such as solvent thermal treatment, as well as aerogels/hydrogels. Sol–gel technology in China holds vast potential for development. We anticipate that sol–gel technology will be widely applied in more fields, especially playing a more crucial role in addressing major issues such as energy, environment, and health. In the future, it will continue to make outstanding contributions to human well-being and technological advancement.

Keywords sol–gel; China; history of development; nanomaterials