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直写 3D 打印陶瓷基多孔结构的研究进展

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摘 要: 陶瓷基多孔结构既继承致密陶瓷材料耐高温、电绝缘、化学稳定的优异性能, 又兼具多孔结构低密度、高比表面积、低热导率的独特优势, 已被广泛应用于隔热、骨组织工程、过滤及污染物清除、电子元器件等领域。但是, 陶瓷基多孔结构的传统成孔方法在宏观尺度创造复杂几何外形与微纳尺度调控孔结构形态方面仍面临巨大挑战。近几十年来, 研究人员一直致力于创新陶瓷基多孔结构的加工成型方法, 以直写 3D 打印为代表的增材制造技术成为当前研究的热点, 并迅速发展出一系列成熟理论与创新方法。本文首先概述了陶瓷基多孔结构的传统成孔方法与增材制造成孔方法, 进一步详细介绍了直写组装成孔工艺过程, 主要包括假塑性墨水配方、固化策略、干燥及后处理, 分析了传统成孔方法与直写 3D 打印二者的组合技术在构筑陶瓷基多级孔结构方面的可行性, 总结了直写 3D 打印技术在制造复杂陶瓷基多孔结构领域的新观点、新进展和新发现, 最后结合陶瓷基多孔结构实际应用现状对直写 3D 技术的未来发展与挑战进行了展望。

关 键 词: 增材制造; 直写 3D 打印; 陶瓷; 多孔材料; 功能应用; 综述

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Direct-ink-writing 3D Printing of Ceramic-based Porous Structures: a Review

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Abstract: Ceramic-based porous structures not only inherit the excellent properties of dense ceramic materials such as high-temperature resistance, electrical insulation, and chemical stability, but also have unique advantages similar to porous structures, including low density, high specific surface area, and low thermal conductivity. They show great potential in various applications, such as thermal insulation, bone tissue engineering, filtration and pollutants removal, and electronic components. However, there still exist some challenges for shaping complex geometries on the macro-scale and adjusting pore morphologies on the micro- and nano-scale through the conventional preparation strategy of ceramic-based porous structures. In recent decades, researchers have been devoting themselves to developing novel manufacturing techniques for ceramic-based porous structures. The direct-ink-writing 3D printing, as one of the representative additive manufacturing technologies, has become a current research hotspot, rapidly developing a series of mature theories and innovative methodologies for fabricating porous structures. In this work, the conventional strategies and additive manufacturing strategies for obtaining porous structures were firstly summarized. The

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direct-write assembly processes of pore structures were further introduced in detail, mainly including pseudoplastic ink formulation, solidification strategy, drying, and post-treatment. Meanwhile, the feasibility of direct-ink-writing 3D printing technologies combined with conventional manufacturing strategies in constructing ceramic-based hierarchical pore structures was analyzed emphatically. The new perspectives, developments, and discoveries of direct-ink-writing 3D printing technologies were further summarized in the field of manufacturing complex ceramic-based porous structures. In addition, the developments and challenges in the future were prospected according to the actual application status.

Key words: additive manufacturing; direct-ink-writing 3D printing; ceramic; porous material; functional application; review

陶瓷基多孔结构具有低密度、高比强度、高比表面积、电绝缘以及热/化学稳定等优异特性[1-4], 是应用于保温隔热、骨组织工程、过滤及污染物去除、电子器件等领域的理想材料[5-14]。其中, 孔结构参数, 如孔隙率、孔径、孔形状、孔分布及连通性, 对陶瓷基多孔结构的功能应用产生决定性影响。目前, 已有多种传统方法用于制造陶瓷基多孔结构, 包括部分烧结法[15]、直接发泡法[16-17]、牺牲模板(复制模板)法[18-20]、溶胶-凝胶法[21-22]和冷冻浇筑法[23]。然而, 这些传统方法通常受限于具体制备条件, 使陶瓷基多孔结构产品存在不同程度的结构形态与性能缺陷。例如, 烧结法中模压成型导致最终产品孔隙率小于 50%[1]; 直接发泡法难以生产复杂外观形状的陶瓷基多孔产品[24-25]; 牺牲模板(复制模板)法通常采用有机物作为模板, 燃烧或热解有机模板一般会对陶瓷基多孔结构造成一定程度的污染[19-20]; 溶胶-凝胶法主要是针对高化学活性的胶体颗粒或先驱体溶液实施凝胶成孔, 它通常依赖超临界干燥技术获得纳米孔结构[21-22]; 冷冻浇筑法只适用于制备定向排列的微米级孔[23]。

3D打印, 又称增材制造, 是一种依托计算机辅助设计制作数字模型、自下而上逐层累积材料构建目标对象的技术[26-30]。如图 1 所示, 现已有多种 3D 打印方法用于制备多孔结构[31], 其中, 陶瓷基多孔结构的增材制造方法主要包括: 紫外光或激光固化墨水的光固化 3D 打印[32-35]、喷洒墨水或黏结剂的喷射 3D 打印[36-39]和挤出假塑性墨水的直写 3D 打印[40-42]。相比于传统减材制造, 3D 打印技术在构建陶瓷基多孔结构方面具有两点优势: 一是宏观尺度整体化成型复杂几何结构与微纳尺度精细调控孔结构参数[27], 体现出 3D 打印技术对陶瓷基多孔结构设计的灵活性; 二是增材制造过程具有制备周期短、成本低、可持续性高、资源集约、无额外模具辅助等特点, 可以有效避免陶瓷脆性缺陷导致多孔几何体出现开裂、破碎等现象。

在上述几种增材制造方法中, 直写 3D 打印技术以其低成本、简单设备构造、强大材料兼容性等

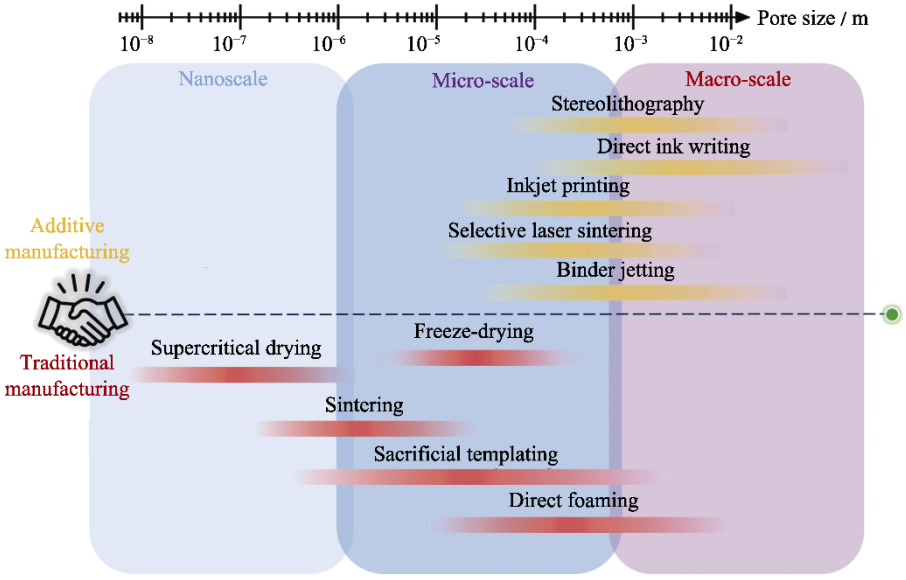

图 1 增材制造技术与传统制造技术互补制备多孔结构[4]

Fig. 1 Complementarity of additive manufacturing and traditional processing for fabricating porous structures[4]

优势而备受学术界和工业界青睐[29,43-44], 它能够以高尺寸分辨率、高形状保真度、高结构复杂性的方式进行孔结构的设计、构造与组装, 为精准、可控、编程化制造陶瓷基多孔结构提供了良好解决方案。本文从现有陶瓷基多孔结构的制备方法出发, 详细介绍直写 3D 打印技术的墨水配方、固化策略、干燥及后处理过程, 重点分析组合传统成孔方法的直写 3D 打印技术在构筑陶瓷基多级孔结构方面的可行性, 并总结陶瓷基多孔结构产品的应用研究进展。

1　陶瓷基多孔结构的直写 3D 打印技术

1997 年, Cesarano 和 Grieco 首次报道了直写 3D 打印技术, 并将其命名为“自动浇筑”技术[45]。从此, 直写 3D 打印技术得到蓬勃发展, 不仅能够在宏观尺度赋予陶瓷基多孔结构定制几何特征的外型, 还能在微观尺度调控孔结构特征。本文将着重介绍直写组装成孔工艺过程和 3D 打印多级孔陶瓷结构这两方面取得的新技术、新进展。

1.1　直写组装成孔工艺过程

陶瓷基多孔材料的直写组装成孔工艺过程主要包括: 假塑性墨水配方、固化工艺、干燥及后处理。其中, 干燥及后处理过程主要包括去除溶剂、转化陶瓷孔和热解有机物等, 可直接借鉴传统陶瓷基多孔材料的制备工艺。由此可见, 直写 3D 打印陶瓷基多孔结构所面临的困难与挑战主要集中于前两个工艺过程。

1.1.1　假塑性墨水配方

直写 3D 打印技术作为一种基于挤出墨水的逐层制造方式(图 2(a)), 它要求陶瓷基墨水具有假塑性(剪切变稀)非牛顿流体特性。墨水的黏度随着剪切速率的增加而降低(图 2(b)), 二者之间的关系可用幂函数(公式(1))表示[29]:

$$\eta = K\dot{\gamma}^{n-1} \tag{1}$$

其中, η 为黏度, K 为流动稠度常数, $\dot{\gamma}$ 为剪切速率, n 为流动指数。对于剪切变稀的假塑性流体, $0<n<1$; 相反, 剪切增稠流体, $n>1$。除黏度外, 储能模量(G')与损耗模量(G'')的比值大于 1 是确保墨水挤出打印成型的另一重要指标。图 2(c)展示了墨水在挤出打印期间的理想模量响应[28], 并对应于墨水流经喷嘴时的不同区域。在喷嘴内部(区域 1), 剪切应力高于屈服应力(τ_0), G'低于 G'', 墨水呈现屈服流动态; 在喷嘴外(区域 2), 外作用力消除, G'高于 G'', 墨水转变为弹性固体态, 能够克服自身重力实现自支撑[46], 从而避免了墨水丝束堆积的打印孔结构在静置时发生结构坍塌。

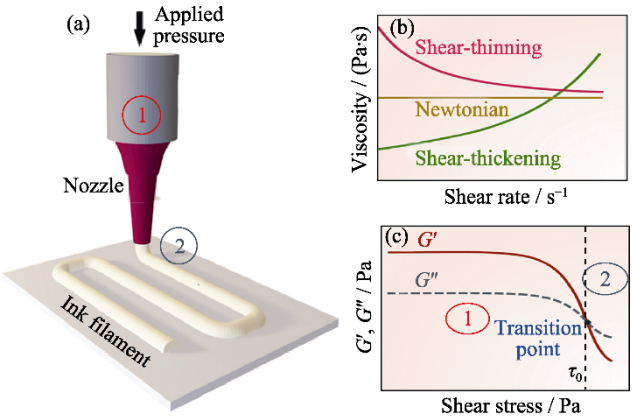

图 2　直写 3D 打印技术

Fig. 2　Direct-ink-writing 3D printing technology

(a) Schematic illustration of the ink extrusion process[29]; (b, c) Rheological behavior of pseudoplastic inks[28]

陶瓷基多孔结构通常以价格低廉的陶瓷粉末作为基础原料, 但因其表面化学惰性, 多数陶瓷基粉末溶液难以获得理想的假塑性流变特性。为此, 增稠剂对于实现墨水配方假塑性流变行为十分必要。如表 1 所示, 常用的增稠剂主要为各类纤维素[47-49]、聚乙烯亚胺(PEI)[48]、聚乙烯醇(PVA)[41-42,50]、聚丙酰胺(PAM)[47]、聚乙烯缩丁醛(PVB)[51]、聚乙二醇(PEG)及其衍生物[51-52]、聚甲基丙烯酸甲酯(PMMA)[53]、Pluronic F127[54-56]、石墨[57]、气相氧化硅粉[41-42]、氧化硅气凝胶粉[50]等。上述物质普遍含有羟基官能团, 能够在水溶液中自发相互作用形成氢键交联网络, 使墨水在静置状态下表现出凝胶态或泥膏态弹性固体行为; 在剪切力作用下, 氢键交联结构发生解离, 墨水表现出流动态黏性液体行为。值得注意的是, 复配增稠剂可显著改善氢键交联结构的可逆性响应, 确保陶瓷基墨水具有良好的挤出打印成型性。

基于墨水流变性能调控挤出打印参数是预防增材制造陶瓷基多孔结构过程中出现打印孔结构缺陷、形状失真的关键措施, 这些打印参数主要包括挤出速度(或压力)、打印速度和喷嘴尺寸。其中, 流经喷嘴的最大剪切速率主要与墨水的体积流速和喷嘴尺寸有关, 可用如下公式表示[58]:

$$\dot{\gamma}_{\max} = \frac{4Q}{\pi r^3} \tag{2}$$

其中, r 是喷嘴半径, Q 是体积流速, 由公式 $Q=vr^2$ 计算所得, v 是打印速度。由公式(2)可知, 小喷嘴、高打印速度通常会使墨水在喷嘴内部产生高剪切速率, 一旦超过极限剪切速率就会破坏墨水氢键交联结构并产生液滴化现象, 这不利于墨水丝束连续挤

出和获得微米级尺度孔结构。因此, 为确保陶瓷基多孔结构的形状保真度, 直写 3D 打印的喷嘴尺寸通常大于 200 μm, 打印速度控制在 20 mm·s^{-1} 以下[29]。此外, 在已知喷嘴规格和施加挤出压力条件下, 喷嘴内部的剪切应力可用公式(3)进行估算:

$$\tau = \frac{\Delta P}{2L} r \tag{3}$$

其中, ΔP 是施加在喷嘴上的压力, r 是从喷嘴中心到边缘的径向长度(喷嘴半径), L 是喷嘴长度。在达到屈服点之前, 小尺寸喷嘴通常需要在更大作用力下才能使墨水发生屈服流动。

此外, M'Barki 等[59]提出了屈服应力与打印样品自重和毛细管张力之间的关系:

$$\tau_0^{\mathrm{dyn}} = \gamma R^{-1} + \rho g h \tag{4}$$

其中, τ_0^{dyn} 是动态屈服应力, γ 是表面张力, R 是喷嘴直径, $\rho g h$ 表示 3D 打印样品的自身的重力压力。由公式(3, 4)可知, 墨水屈服应力过大则需要更大的挤出压力; 墨水屈服应力过小则会导致打印样品无法承受自重和表面张力作用, 限制整体打印高度。因此, 合适的屈服应力通常限定在 10^2~10^3 Pa 范围。

1.1.2 固化策略

固化工艺是直写 3D 打印过程中塑造宏观几何形状和调控微观孔结构形貌的关键步骤。如图 3 所示, 陶瓷基墨水的固化方式主要有三种: 溶液辅助固化、温度诱导固化和光固化。

溶液辅助固化主要依赖于溶液中离子扩散来实现陶瓷基墨水凝胶固化。例如, Smay 等[60]通过 NH_4OH 调节墨水的 pH 至 10.35, 可实现高含量锆钛酸铅墨水凝胶固化。Rebber 等[61]提出在碱性氨液体浴中直写 3D 打印 TiO_2 气凝胶墨水的方法(图 3(a)), TiO_2 气凝胶墨水的固化取决于 OH^-的离子浓度和扩散效率, 该固化策略获得的 TiO_2 气凝胶呈现出优异纳米孔结构(比表面积高达 539 $m^2 \cdot g^{-1}$, 孔径集中分布在 20 nm 左右)。除此以外, 含有海藻酸钠的陶瓷基墨水可在 Ca^{2+}金属离子溶液中形成配位交联凝胶[62-65]。例如, Oliveira 等[63]报道了一种由海藻酸钠与生物活性玻璃为主要原料组成的墨水, 如图 3(b)所示, 经直写组装和浸渍氯化钙溶液后, 海藻酸钠与 Ca^{2+}离子之间形成配位交联凝胶, 并使毫米孔陶瓷支架结构获得良好的形状保真度。

温度诱导固化策略主要包括两类: 热固化和冷固化。所谓热固化是通过加热方式使墨水发生化学反应固化。例如, 本课题组[42, 50]提出一种通用热固化直写 3D 打印纳米孔陶瓷基气凝胶的方法(图 3(c))。在热固化方法中, 尿素作为墨水的温控催化剂, 常温状态下稳定不分解, 确保氧化物陶瓷基墨水能够长时间保存; 当加热温度高于 60 ℃时, 尿素分解并释放碱性氨, 催化氧化物陶瓷基墨水发生缩聚反应, 进而使墨水完全凝胶固化, 经超临界干燥后, 3D 打印气凝胶呈现出典型的纳米孔特征, 性能堪比传统陶瓷氧化物气凝胶。相比于热固化方法, 冷固化本质上等同于冷冻浇筑[28], 该过程通常将墨水沉积于低温平台或将打印样品直接快速冷冻固化, 然后在冷冻干燥过程中升华溶剂得到 3D 打印多孔陶瓷胚体[66-67]。为了方便冷冻固化, 墨水通常以水作为溶剂[23,68], 高冰点温度的甘油、叔丁醇、樟脑、萜烯等溶剂[23,69-74]也常被用作冷冻致孔溶剂。例如, Moon 等[70]通过冷冻浇筑含樟脑溶剂墨水制备了氧化铝多孔支架结构。

光固化是指陶瓷基墨水在特定光源照射下发生自由基聚合反应生成坚固的聚合物网络, 光源多为紫外光[75-79]。在直写 3D 打印过程中, 光固化通常发生在挤出墨水丝束后, 并在瞬间到几分钟内完成, 这要求墨水沉积与光固化过程在时间上存在紧密的协同性[80]。为此, 假塑性墨水配方除必要的功能陶瓷先驱体或粉体外, 还需要含有光敏单体或低聚物、光引发剂以及其它有机添加剂。如图 3(d)所示, Jonhson 等[79]将氧化硅粉、乙二醇、聚乙二醇二丙烯酸酯、光引发剂等原料混合获得了泥浆状可光固化陶瓷基墨水, 采用逐层交替实施墨水沉积与光固化的方法制造了陶瓷基多孔支架。相比于溶剂辅助固化和温度诱导固化方法, 光固化策略使 3D 打印多孔结构的力学强度更高[81], 在一定程度上抑制了收缩和开裂, 有助于陶瓷基多孔结构实现高结构完整度和高形状保真度。

1.1.3 干燥及后处理过程

固化后, 3D 打印样品需要经过干燥及后处理过程才能获得定制孔结构特征。常用干燥方法主要包括超临界干燥、冷冻干燥和常压干燥[26,28,82], 干燥过程中的温度、压力参数变化如图 4 所示。其中, 超临界干燥主要用于制备陶瓷基纳米孔结构。在超临界状态下, 液体与气体之间的相界面消失, 溶剂表面张力及其所导致的毛细管应力明显降低[83], 有效抑制了纳米孔结构坍塌[84], 进而确保 3D 打印样品获得高孔隙率、高比表面积、集中孔径分布等纳米多孔气凝胶特征。但是, 超临界干燥工艺的显著不足是设备成本高、能耗高并且需要多次溶剂置换[85], 这在一定程度上抑制了陶瓷基多孔结构的生产效率与市场占有率。冷冻干燥工艺是在低压状态下将冷冻溶剂固体升华为气体[66-67], 该过程绕过液体相区域而直穿固–气相界面, 避免了毛细管力作用[23]。在直写 3D 打印技术中, 冷固化与冷冻干

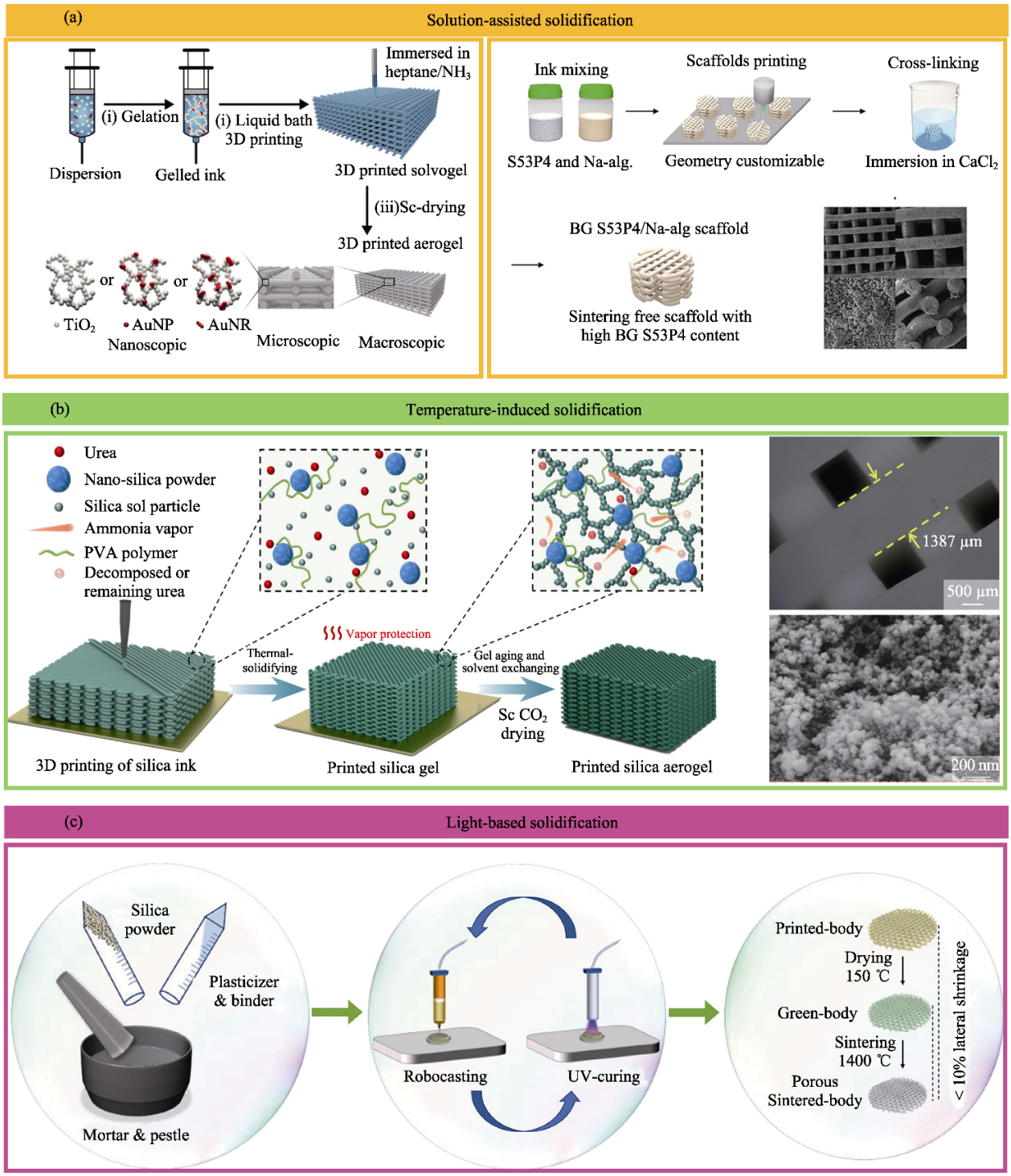

图 3　陶瓷基墨水的固化方法

Fig. 3　Solidification strategies of ceramic-based inks

(a) Solution-assisted solidification[61,63]; (b) Temperature-induced solidification[42,50]; (c) Light-based solidification[79]

燥相结合，在低温环境下连贯实施[86]，冷冻溶剂的冰晶效应使 3D 打印样品内部形成微米孔，控制冷冻温度、压力和冷冻速率等参数，可调控最终产品的孔结构特征[87-88]。与超临界干燥相比，冷冻干燥技术具有便宜设备、操作简便、安全性高等优势，但存在扩展性相对较差与能耗问题。常压干燥是一种高效、低廉的干燥方法，一般不涉及高精密设备，通常要求低表面张力溶剂在常压环境中直接挥发成气体。受制于毛细管力作用，多孔结构在干燥过程中存在高体积收缩现象，导致 3D 打印产品的形状保真度相对较差。为抑制常压干燥过程中出现较大尺寸收缩与开裂，可依赖直写 3D 打印技术设计特定孔道的镂空结构[89-92]，增大打印结构与空气的接触面积，从而实现均匀溶剂挥发[40,93]。

表 1　代表性陶瓷基多孔结构的孔结构特征和墨水配方的流变性能及其打印参数

Table 1　Pore structure characteristics of representative ceramic-based porous structures and rheological properties and printing parameters of ink formulations

Sample	Ink formulation	Content	Pore structure characteristics	Rheological behaviors	Printing parameters	Ref.
Piezoelectric ceramic	Lead zirconate titanate, PVB, PEG, dibutyl phthalate, triethyl phosphate xylene, and ethanol	79.5% (in mass)	Pore type: printed pore; Pore shape: rectangle pore; Pore size: ~600 μm;	η: ~10^3 Pa·s; τ_0: 8–50 Pa	Nozzle: 260, 210 μm	[51]
Al_2O_3 ceramic	Alumina powder, PAM, Darvan 821A, methylcellulose, PEI, Pluronic F127, water	35%–55% (in vol)	Pore type: hierarchical pore; Pore shape: rectangle and spherical pore; Porosity: 73%–79%	η: 10^2–10^4 Pa·s; G'_0: 1.1×10^4 Pa; G''_0: 7×10^3 Pa; τ_0: 2×10^2–15×10^2 Pa	Extrusion pressure: 80–240 kPa; Printing velocity: 2 mm·s^{-1}; Nozzle: 510 μm	[48]
	α-Al_2O_3 powder, Pluronic F127, water	60%–75% (in mass)	Pore type: printed pore; Pore shape: rectangle and hexagonal pore; Porosity: 50%–60%	G'_0: 2.6×10^4–5.8×10^7 Pa; G''_0: 4.0×10^4–4.9×10^6 Pa; τ_0: 1.7×10^3–4.3×10^3 Pa	Nozzle: 580 μm	[56]
Yttria stabilized zirconia ceramic	Yttria stabilized zirconia nanoparticle, polyethylene glycol diacrylate, Luperox®231	55%–70% (in mass)	Pore type: hierarchical pore; Pore shape: rectangle and spherical pore	η: 1×10^2–7×10^2 Pa·s; G'_0: 1×10^5–16×10^5 Pa; τ_0: 10^2–10^3 Pa	Extrusion pressure: 103–172 kPa; Printing velocity: 3 mm·s^{-1}; Nozzle: 250–1190 μm	[52]
hBN ceramic composite	Hexagonal boron nitride, polysilazane resin	20%–43% (in vol)	Pore type: printed pore; Pore shape: hexagonal pore	G'_0: 7.6×10^4 Pa; τ_0: 4.27×10^2 Pa	Printing velocity: 25 mm·s^{-1}; Nozzle: 410 μm	[94]
Hydroxyapatite scaffold	Hydroxyapatite powder, hydroxypropyl methylcellulose, water	~80% (in mass)	Pore type: hierarchical pore; Pore shape: rectangle and spherical pore; Porosity: 5%–55%	–	Extrusion pressure: 100–200 kPa; Printing velocity: 10 mm·s^{-1}; Nozzle: 200 μm	[49]
Porous SiC ceramic	Metakaolin, silica sol, SiC powder, graphite powder, sodium dodecyl sulfate, water	–	Pore type: hierarchical pore; Pore shape: hexagonal and irregular pore	η: >10^5 Pa·s; G'_0: 10^4–10^5 Pa; τ_0: 10^2–10^3 Pa	–	[57]
Si_2N_2O ceramic foam	Silicon nitride powder, fumed silicon oxide, yttrium oxide powder, aluminum oxide powder, PVA, yeast, water	~46% (in mass)	Pore type: hierarchical pore; Pore shape: hexagonal and irregular pore; Porosity: 61%–71%	η: 1.5×10^2–2.8×10^2 Pa·s; G'_0: ~10^5 Pa, G''_0: ~10^4 Pa; τ_0: 4.0×10^2–1.4×10^3 Pa	Nozzle: 600 μm	[41]
Polymer-based SiOC ceramic	Polymethylsiloxane, PMMA particle, isopropanol	50%–80% (in vol)	Pore type: hierarchical pore; Pore shape: rectangle and spherical pore; Porosity: 72%–87%	G'_0: 5.6×10^3 Pa τ_0: 24 Pa	Extrusion pressure: 300–600 kPa; Printing velocity: 5–10 mm·s^{-1}; Nozzle: 400 μm	[53]
SiO_2 aerogel	Silica aerogel powders, fumed silica powders, silica sols, PVA, glycerol, water	19%–28% (in mass)	Pore type: printed pore and nanopore; Pore shape: rectangle and spherical pore; Pore size: nanopore of ~37 nm	η: 2×10^4–1×10^5 Pa·s; G'_0: 10^4–10^5 Pa; τ_0: 5×10^2–5×10^5 Pa	Extrusion velocity: 10–20 mm^3·s^{-1}; Printing velocity: 4–12 mm·s^{-1}; Nozzle: 840–1350 μm	[50]
Al_2O_3-SiO_2 aerogel	Boehmite, fumed silica, silica sols, PVA, water	21%–29% (in mass)	Pore type: printed pore and nanopore; Pore shape: rectangle and spherical pore; Pore size: nanopore of ~25 nm	η: 2.3×10^5 Pa·s; G'_0: 1.2×10^5 Pa; τ_0: 2.3×10^3 Pa	Extrusion velocity: 10–30 mm^3·s^{-1}; Printing velocity: 4–15 mm·s^{-1}; Nozzle: 840–1350 μm	[42]
TiO_2-SiO_2 aerogels	Rutile, fumed silica, silica sols, PVA, water	26%–32% (in mass)	Pore type: printed pore and nanopore; Pore shape: rectangle and spherical pore; Pore size: nanopore of ~37 nm	η: 2.0×10^5 Pa·s; G'_0: 6.2×10^4 Pa; τ_0: 2.0×10^3 Pa	Extrusion velocity: 10–30 mm^3·s^{-1}; Printing velocity: 4–15 mm·s^{-1}; Nozzle: 840–1350 μm	

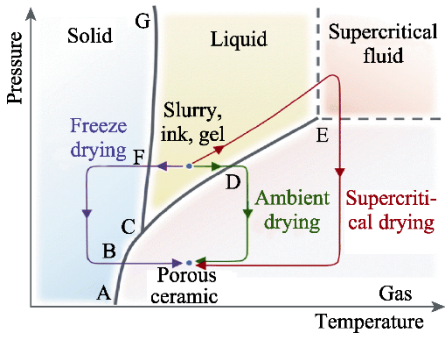

图 4　不同干燥技术的温度和压力变化[28]

Fig. 4　Parameter variation of temperature and pressure for different drying processes[28]

后处理工艺多发生在干燥过程后, 以热处理方式为主。在直写 3D 打印过程中, 后处理的目的主要在于: 一是去除墨水配方中预留有机成分, 原位生成可控模板孔, 进一步丰富材料的孔结构特征; 二是通过陶瓷化方式改善多孔结构骨架的稳固性以及力学强度。相较于块体多孔结构, 3D 打印镂空多孔结构具有毫米级、微米级规则排列的孔道结构, 为热解有机物产生的小分子气体提供了快速逸散通道, 有利于在热处理过程中防止有机残留物对陶瓷基多孔结构造成污染。

1.2　直写 3D 打印陶瓷基多级孔结构

尽管直写 3D 打印技术在制造陶瓷基多孔结构方面取得了巨大的进步, 但在制造亚微米级、纳米级多孔结构方面仍存在一定局限性。鉴于直写 3D 打印技术具有成本低、设备构造简单和墨水兼容性强等优势[4,29,43], 研究人员将该技术与直接发泡法、冷冻浇筑法、牺牲模板法、溶胶–凝胶法等传统成孔方法相组合, 用于制备多级孔陶瓷结构。这些组合传统成孔方法的直写3D打印技术能够跨尺度制造纳米级孔到毫米级孔, 精准调控孔形状、孔尺寸、孔规则度、孔连通性以及填充度等特征, 展现出极强的定制孔结构特性。

1.2.1　组合直接发泡法的直写 3D 打印技术

直接发泡法是一种将空气注入悬浮液或均相溶液中获得气泡结构并经高温烧结转化为高强度多孔陶瓷的方法, 该方法具有简单、廉价、快速等特点, 制备的陶瓷材料多呈现大孔结构, 孔隙率为 40%~97%[24]。2016 年, Minas 等[40]将直接发泡工艺与直接 3D 打印技术相结合(图 5(a, b)), 实现了氧化铝多级孔结构增材制造。Muth 等[95]将组合发泡工艺的直写 3D 打印技术命名为“直接泡沫书写”, 并使该技术得到业内广泛采纳与借鉴[89, 96-98]。实施组合发泡工艺的直写 3D 打印技术的关键在于: 调控表面活性剂浓度实现陶瓷浆料气泡稳定, 并使其自身获得假塑性流变性能以满足挤出打印成型要求(表 1)。根据这一原则, 相关学者成功将该组合直写 3D 打印技术应用于制造 TiO_2[97]、Al_2O_3-MgO-SiO_2[98]、勃姆石[99]等多级孔陶瓷材料。

1.2.2　组合冷冻浇筑法的直写 3D 打印技术

冷冻浇筑法是定向制造微米孔的有效方法[100], 该方法也是固化陶瓷基墨水的可替换方法, 通常与冷冻干燥过程联用制备超低密度多孔陶瓷[23]。如图 6(a)所示, Moon 等[70]将冷冻浇筑工艺与直写 3D 打印技术相结合, 制备了具有毫米级与微米级双尺度定向孔的氧化铝多孔支架结构。值得一提的是, 墨水配方选用高冰点温度的萘烯作为溶剂, 可在室温环境中实现萘烯结晶成孔, 冷冻干燥形成类似于天然骨组织的分层多级孔结构(图 6(b)), 经高温烧结后, 该结构抗压强度可达到 9.5 MPa。

1.2.3　组合牺牲模板法的直写 3D 打印技术

牺牲模板法广泛用于合成有机物衍生多孔陶瓷材料[101-103]。相比于无机陶瓷粉体, 有机物因其含有丰富活性基团, 更有利于墨水获得良好的流变性能。与此同时, 有机物本身也被视为一种优良的陶瓷造孔剂。因此, 牺牲模板工艺与直写 3D 打印技术相组合也是构筑陶瓷基多级孔结构的可行方法。例如, Huang 等[53]将组合牺牲模板法的直写 3D 打印技术应用于制造多级孔的 SiOC 陶瓷构件, 如图 7(a)所示, 聚甲基硅氧烷树脂与 PMMA 微珠在异丙醇溶剂中混合得到假塑性墨水, 通过直写 3D 打印技术构筑毫米孔支架结构, 经交联和热裂解过程转化为 SiOC 陶瓷, 在上述制备过程中, 粒径 0.46~50 μm 范围的 PMMA 微珠热分解为小分子气体, 形成大小不一的微米级和纳米级球形孔(图 7(b))。此外, Yang 等[104]开发了一种超分子胶束凝胶墨水, 并通过直写 3D 打印技术制备了多级孔氧化铝陶瓷结构, 如图 7(c)所示, 三种超分子胶束作为自牺牲模板剂可精准调控孔尺寸与孔排列组合。

1.2.4　组合溶胶–凝胶法的直写 3D 打印技术

溶胶–凝胶法是制备纳米多孔陶瓷基材料的典型方法, 该方法多依赖超临界干燥技术, 用以防止溶剂去除过程中发生纳米孔结构坍塌[22]。因此, 很多研究人员将组合溶胶–凝胶工艺的直写 3D 打印技术用于制造气凝胶材料[28,42,50,60,80,105-106]。例如, Zhao 等[105]首次报道了纯氧化硅气凝胶的小型化增材制造, 并展示了具有微米孔与纳米孔排列组合的氧化硅气凝胶支架结构(图 8(a))。本课题组[42,50]

实现了不同组分氧化物陶瓷基气凝胶支架的直写组装。Rebber 等[61]采用直写 3D 打印技术制备了 TiO_2 气凝胶支架，并将其成功应用于光热转换(图 8(b))。

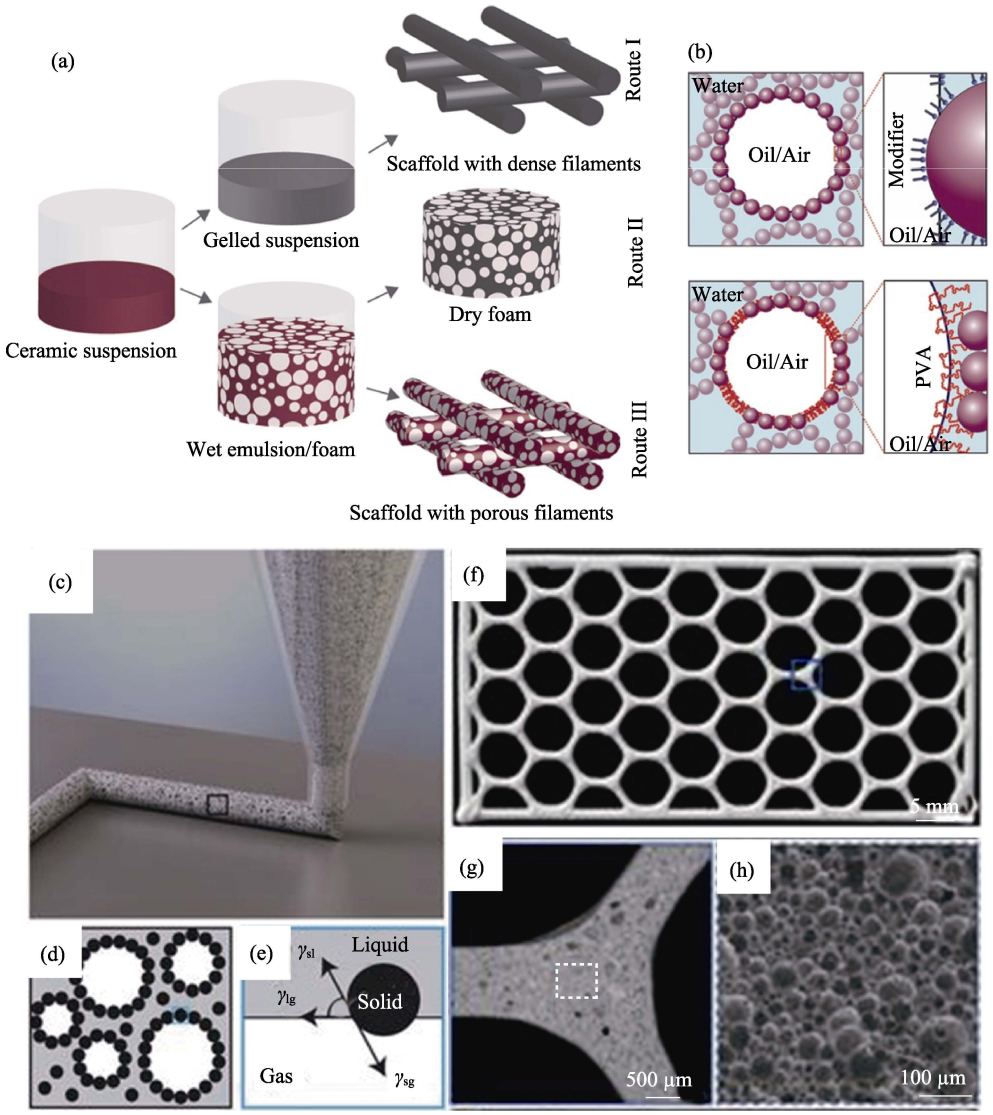

图 5 组合直接发泡法的直写 3D 打印技术

Fig. 5 Direct-ink-writing 3D printing technology integrated with direct foaming methods

(a, b) Process schematic diagram of direct foam writing for porous ceramic-based structures[40]; (c-h) Morphologies of honeycomb ceramic with hierarchical pore structures[95]

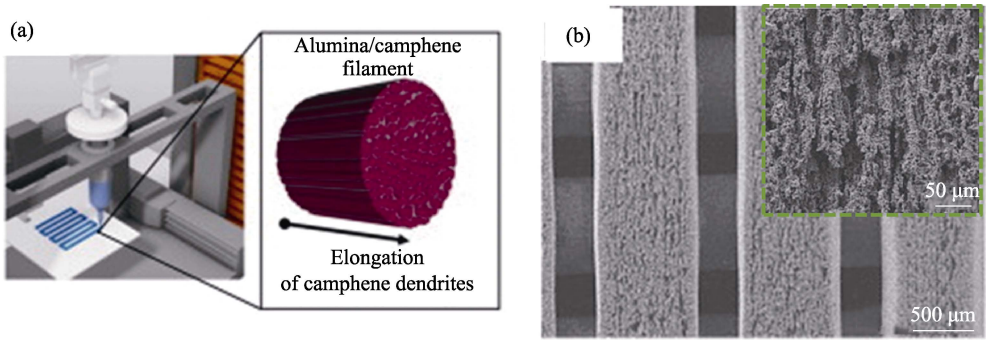

图 6 组合冷冻浇筑法的直写 3D 打印技术及其所制备的多级孔氧化铝支架[70]

Fig. 6 Direct-ink-writing 3D printing technology integrated with freezing casting method and its hierarchical porous alumina scaffold[70]

(a) Schematic illustration of the printing process; (b) Microscopic morphology of hierarchical pore structures

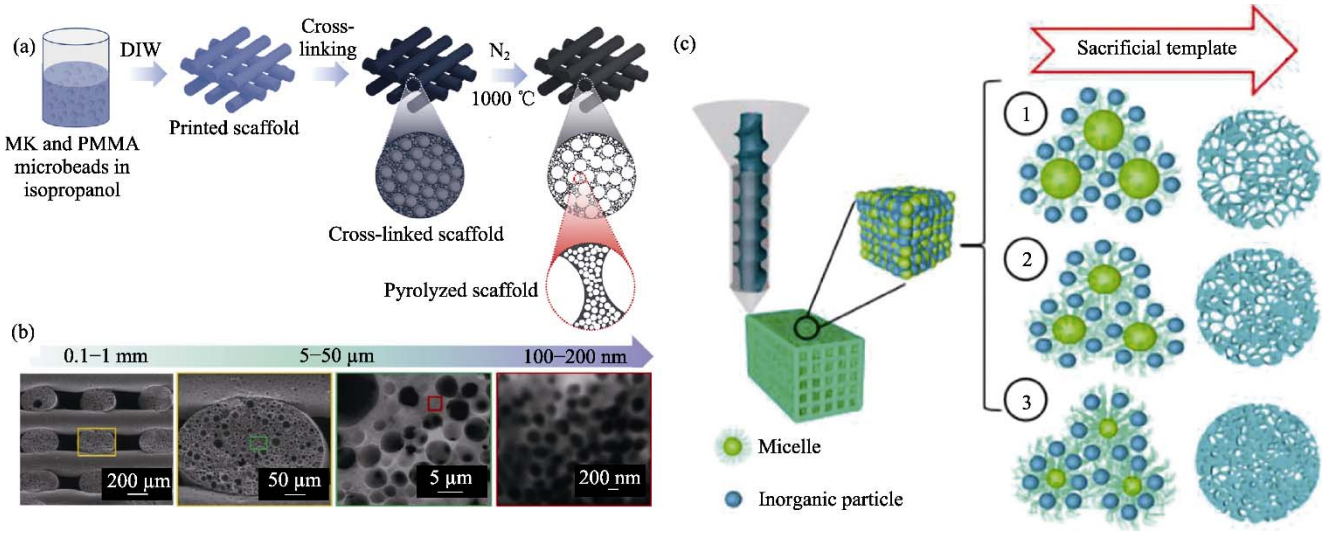

图 7　组合牺牲模板法的直写 3D 打印技术

Fig. 7　Direct-ink-writing 3D printing technology integrated with sacrificial template method

(a, b) Flow chart of preparation of hierarchical porous SiOC ceramic structures[53]; (c) Three sacrificial template methods for 3D-printed ceramics[104]

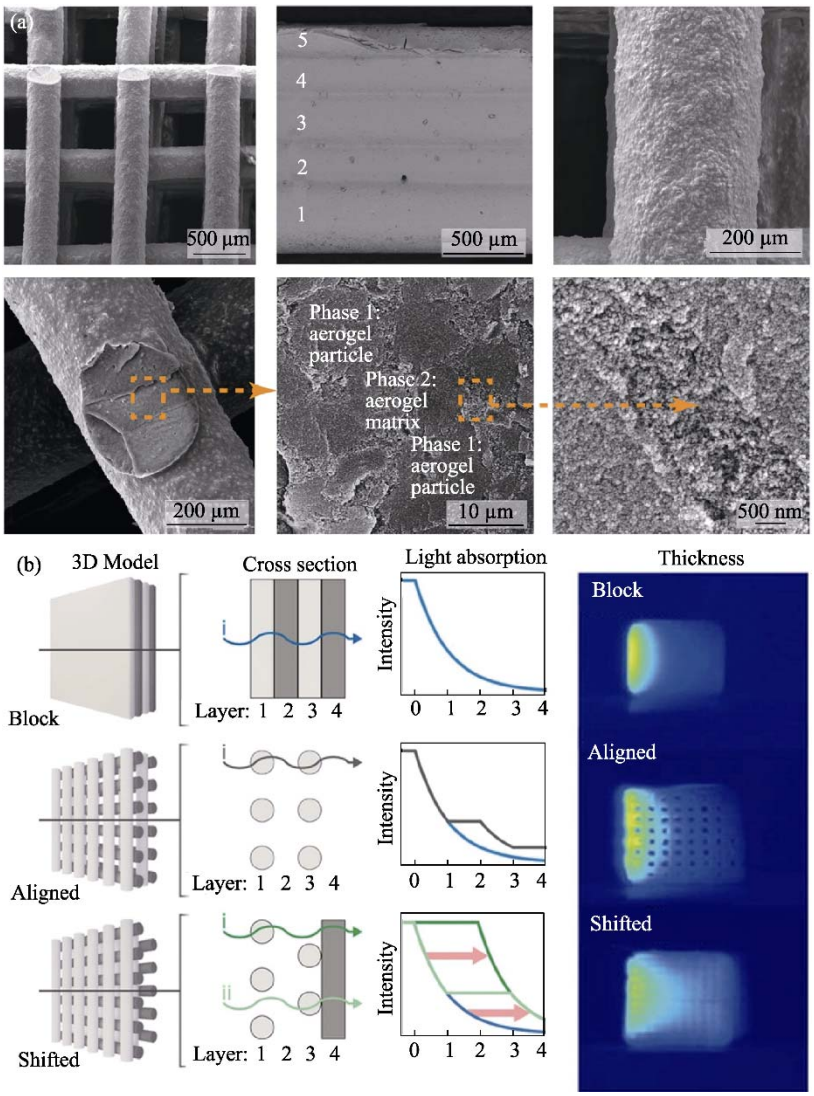

图 8　组合溶胶–凝胶法的直写 3D 打印技术

Fig. 8　Direct-ink-writing 3D printing technology integrated with Sol-Gel method

(a) Morphologies of hierarchical pore structures of SiO_2 aerogels[105]; (b) TiO_2 aerogel scaffolds with different hierarchical pore structures[61]

2 3D 打印陶瓷基多孔结构的应用

直写3D打印技术赋予陶瓷基多孔结构定制的宏观几何体形状与微纳孔结构特征，拓宽了其在各领域的应用潜力，典型应用主要包括以下四个方面：保温隔热、骨组织工程、过滤及污染物清除和电子器件。

2.1 保温隔热

以陶瓷气凝胶为代表的纳米多孔陶瓷基结构具有显著耐高温与低热导率特性，是保温隔热的理想材料。然而，陶瓷基多孔结构存在本征脆性问题，传统制造技术难以实现其宏观几何体按需成型[28,42,50,80]，这导致隔热材料难以匹配安装到目标构件外围，造成相对较差的隔热效果。相比于传统策略，直写3D打印技术为纳米孔陶瓷气凝胶的定制成型提供了可靠方法。例如，Zhao 等[105]直写 3D 打印了纯氧化硅气凝胶，它具有超低热导率(0.0159 $W·m^{-1}·K^{-1}$)，定制外型的氧化硅气凝胶隔热罩可匹配安装至小型电子器件外围，达到高效隔热效果(图 9(c, d))。本课题组[42]提出氧化物陶瓷基气凝胶的热固化直写打印通用方法，开发了形状匹配的气凝胶隔热罩(图9(a, b))，并评估了不同组成氧化物陶瓷气凝胶(SiO_2 气凝胶、Al_2O_3-SiO_2 气凝胶、TiO_2-SiO_2 气凝胶)在高温隔热应用中的潜在可行性。

2.2 骨组织工程

骨缺陷是一个非常棘手的骨科问题，虽然骨组织具有再生能力，但损伤严重时，则必须借助外力进行修复[107]。生物陶瓷(硅酸钙、硅酸锌钙、磷酸钙)是替补骨成分的理想材料，但其研究难点仍在于改善骨移植成骨的方法[108]，这是因为生物陶瓷只有被加工成特定孔道结构和孔形状的支架结构，才能满足骨再生过程中细胞生长、营养迁移、废物清除的要求。直写 3D 技术依据灵活的模型设计与优化，可高效制造仿生生物陶瓷基多级孔骨支架，从而极大促进了骨组织的再生与愈合[109-111]。如图 10 所示，Shao 等[112]证明了直写 3D 打印技术能够精准控制宏观尺度形状和微观尺度结构，制备了可精准匹配下颌缺损部位的生物陶瓷支架，该陶瓷支架具有高弯曲强度(高达 31 MPa)，对生物组织起到良好支撑作

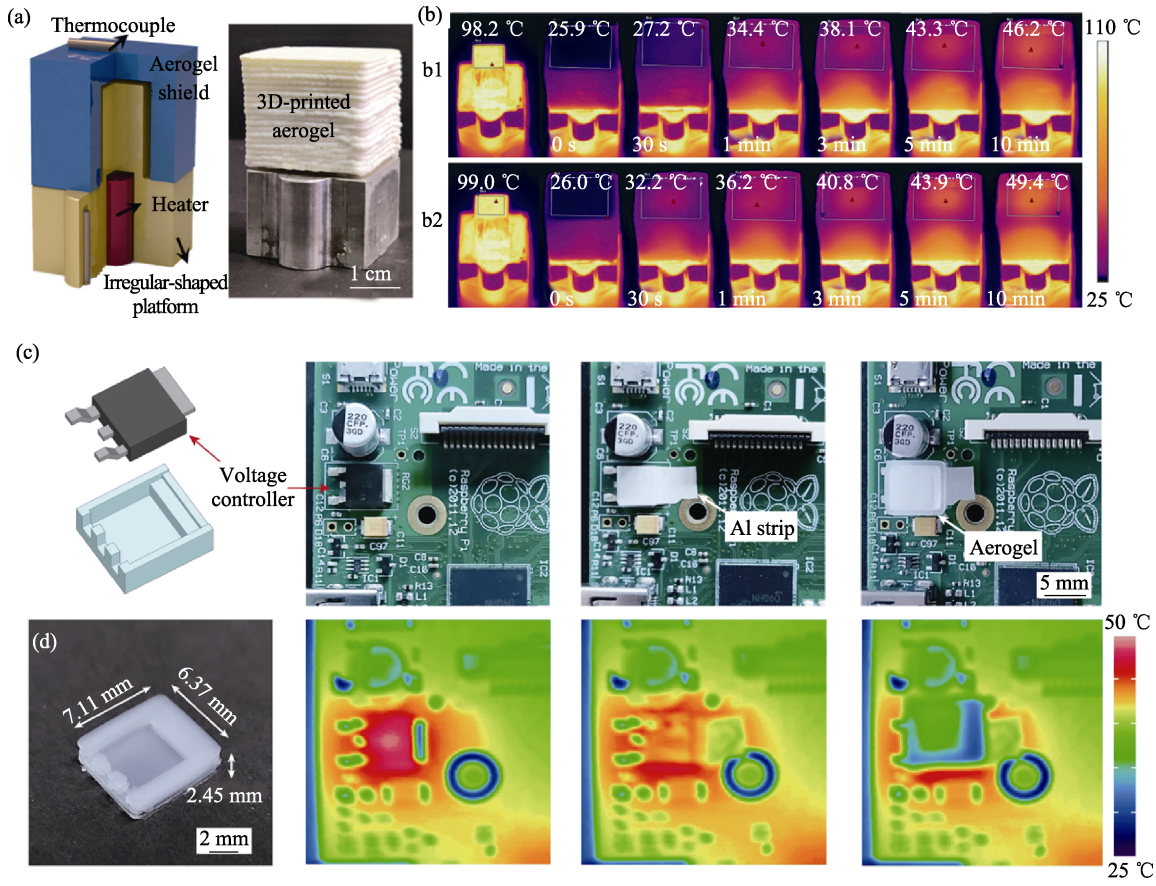

图 9 3D 打印纳米孔陶瓷基气凝胶的隔热应用

Fig. 9 3D-printed nanoporous ceramic-based aerogels for thermal insulation applications

(a, b) Thermal shielding demonstration of 3D-printed Al_2O_3-SiO_2 aerogels[42]; (c, d) 3D-printed SiO_2 aerogels for miniaturized thermal insulation applications[105]

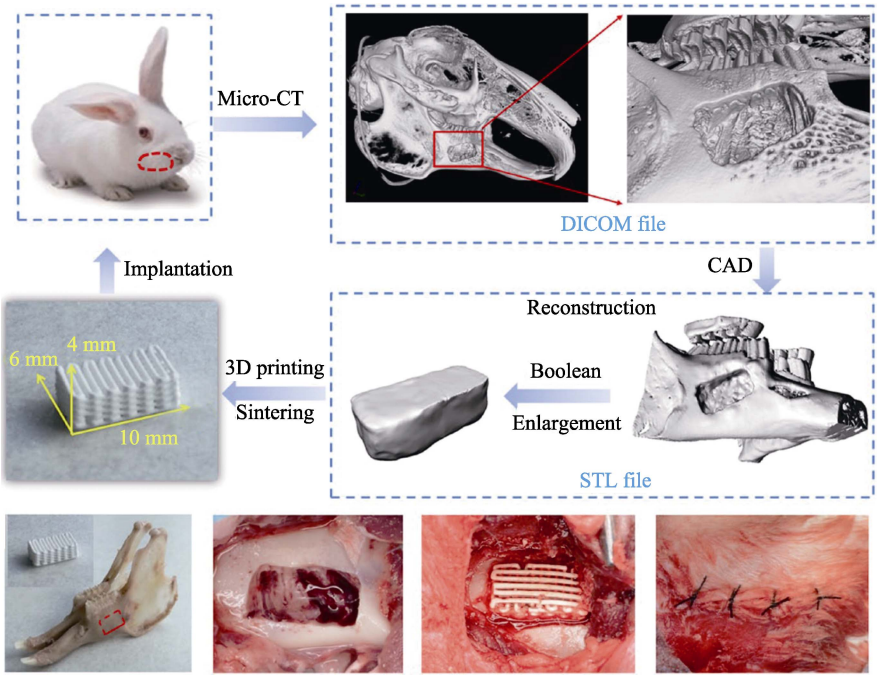

图 10　3D 打印生物陶瓷支架及其骨修复过程的植入图[112]

Fig. 10　3D-printed bioceramic scaffold and its implantation photographs of bone repair processes[112]

用, 有助于短期内实现快速成骨。此外, Zocca 等[113]使用直写3D打印技术制造了高孔隙度多孔硬硅酸钙生物陶瓷, 可使其弯曲强度进一步达到 136 MPa。Elsayed 等[114]通过添加 SrO、MgO、玻璃等填料进一步赋予了生物陶瓷基多孔支架更高的生物相容性与生物活性。

2.3　过滤及污染物清除

受益于良好的化学稳定性, 陶瓷基多孔结构具有可重复使用和长时间耐用等优点, 是高性能催化剂的理想载体, 被广泛应用于过滤及污染物清除[115-117]。借助直写 3D 打印技术, 可分级精准制造多孔陶瓷载体内部输送孔道, 有助于提升化学反应与催化效率[118-120], 加速污染物的去除。例如, Liu 等[115]对 3D 打印氧化硅陶瓷多孔支架表面改性, 原位生长了纳米孔 MOF 结构催化剂, 该多级孔结构过滤器的制备过程如图 11(a)所示, 在处理含有有机染料的污水过程中, 这种多级孔结构过滤器表现出高效的 Fenton 反应效率(图 11(b)), 几乎完全分解有机染料, 去除效率最高可达 99.68%。除去除污染物外, Jonhson 等[78]对 3D 打印氧化硅支架表面进行疏水/亲水修饰, 可使油水混合物在重力驱动流动过程中实现快速油水分离。

2.4　电子器件

陶瓷基多孔结构在电子器件方面的应用主要是以压电陶瓷为材料制备传感器、驱动器、电容器等元器件[51, 122-124]。虽然压电陶瓷的材料成分很大程度上决定了其功能性能, 但是压电陶瓷在某一领域的具体应用还取决于其宏观连接方式[122]。直写 3D 打印为制造压电陶瓷宏观结构形状提供了新方法。Li 等[51]开发了一种直接 3D 打印技术与柔性陶瓷坯体二次成型的组合工艺, 并证明该工艺可以生产复杂的压电陶瓷, 如图 12(a-f)所示, 3D 打印的多孔陶瓷胚体可发生灵活变形, 发生极化后, 样品展示出良好的压电性能, 平均 d_{33} 高达 265 pC/N。Liu 等[121]制备了用于传感器的锆钛酸铅压电复合材料(图 12(g)), 评价了不同打印孔间距对压电性能的影响, 并将多孔压电复合材料应用于水声换能器。此外, Walton 等[125]则借助打印喷嘴的剪切作用实现了浆料内部填料的定向排列, 与填料随机分布的多孔陶瓷相比, 织构排布的多孔压电陶瓷呈现出更好的压电性能。

3　总结与展望

本文系统综述了直写3D打印陶瓷基多孔结构的假塑性墨水配方、固化策略、干燥及后处理等工艺过程, 分析了传统成孔方法与直写 3D 打印二者的组合技术在制造多级孔陶瓷方面的可行性, 总结了直写 3D 打印技术在制造复杂陶瓷基孔结构领域的新观点、新进展和新发现, 最后结合陶瓷基多孔结构实际应用现状展望了直写 3D 技术的未来发展与挑战。

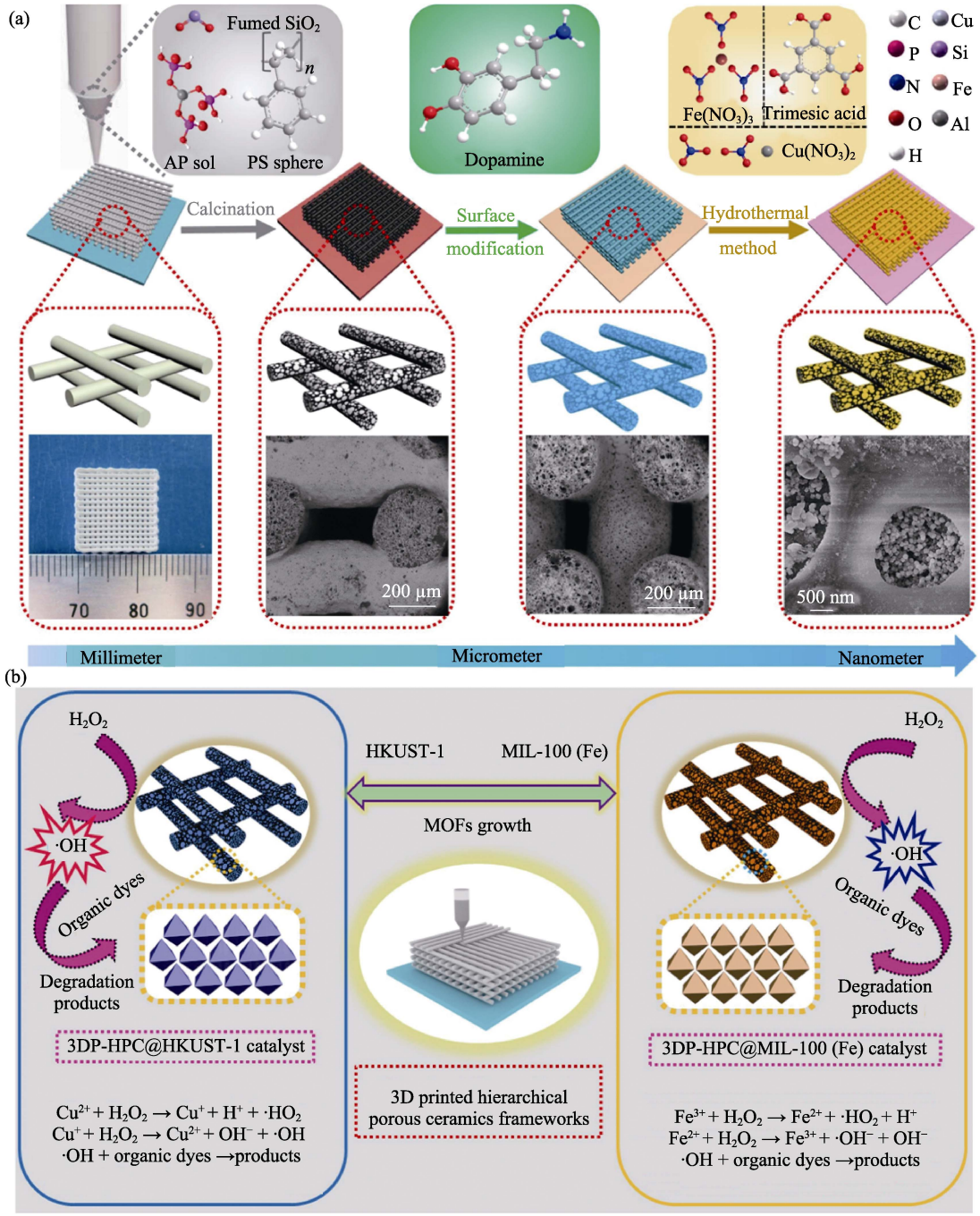

图 11 3D 打印多级孔结构过滤器用于污水净化[115]

Fig. 11 3D-printed filters with hierarchical pore structures for sewage purification[115]

(a) Direct-write assembly process; (b) Pollutant decomposition mechanism

直写3D打印陶瓷基多孔结构的发展主要取决于该技术本身所特有的优势，体现在以下三个方面。一是强大的墨水兼容能力，能够兼容不同种类材料，包括分子级先驱体、纳米颗粒以及粉体，几乎可以实现所有陶瓷材料的增材制造。同时，受益于墨水兼容性，直写 3D 打印技术融入时间维度可继续发展为 4D 打印技术。二是不同墨水配方和可控打印过程赋予陶瓷基多孔结构可调的孔结构特征与功能特性，调节墨水组分、打印参数、固化策略以及组合传统成孔方法，能够调控多孔陶瓷骨架，以满足不同功能应用要求。三是简单的打印设备为后续灵活改装提供了可能，如多喷嘴挤出打印,添加光、热外围辅助设备等，丰富了陶瓷基多孔结构的增材制造方式，有效促进了直写 3D 打印技术的革新与发展。

然而，现阶段直写 3D 打印陶瓷基多孔结构仍存在很多问题与挑战。一是调控墨水流变性能并使其满足挤出要求仍存在一定的难度，还需要深入探索

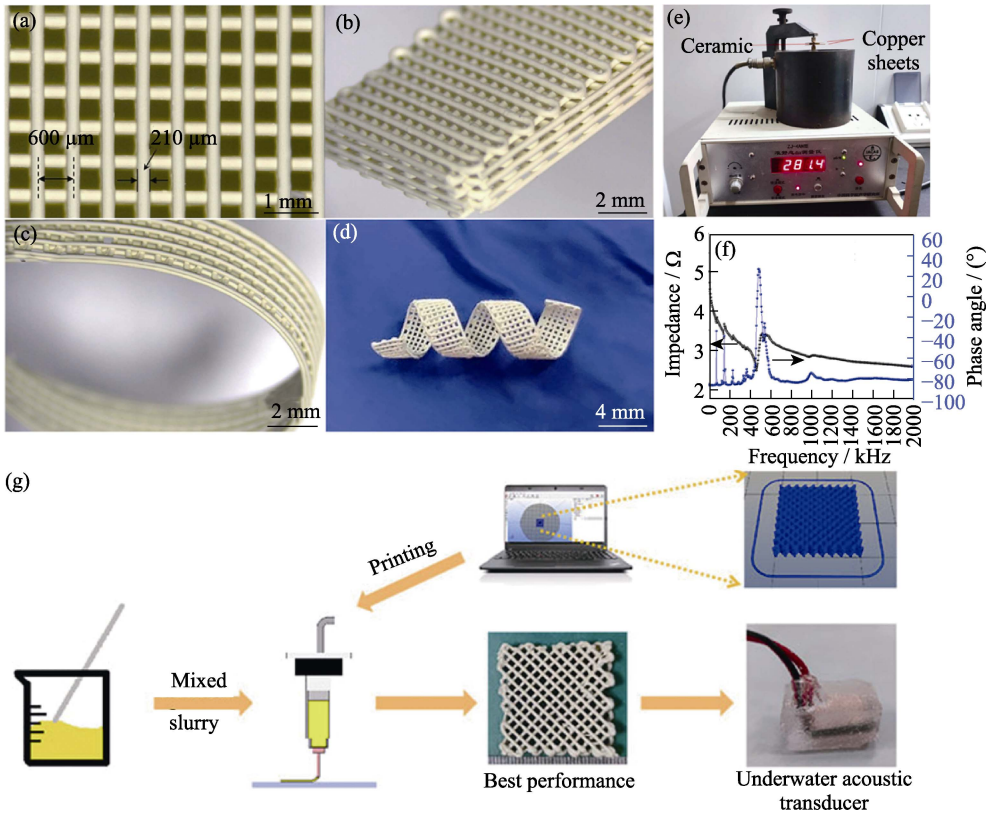

图 12　3D 打印多孔压电陶瓷的结构、性能及其应用

Fig. 12　Structures, performances, and applications of 3D-printed porous piezoelectric ceramics

(a-f) Printed structures and performance characterizations [51]; (g) Direct-ink-writing 3D printing processes of lead zirconate titanate piezoelectric ceramics[121]

墨水配方与流变性能的关系。未来可通过有限元方法构建仿真环境, 模拟不同组分陶瓷基墨水的流变性能, 并根据打印参数优化墨水配方来提高打印效率; 二是受限于陶瓷脆性、低打印速度等因素, 工业化大批量生产高尺寸精度、高结构完整度、高形状保真度的陶瓷基多孔结构仍面临着严重挑战。未来可通过革新直写 3D 打印技术(如: 多喷嘴打印、增强体引入、快速协同固化等)改善现有打印过程中所遇到的问题。

综上所述, 直写 3D 打印技术在制造陶瓷基多孔结构以及其它多孔材料领域有着广阔的应用前景, 凭借独具一格的打印方式、良好的材料兼容性以及灵活的设备改装能力, 可在将来成为尖端制造技术。

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