激光与光电子学进展

中国光学十大进展:三维无机微纳结构的激光加工与应用(特邀)‡

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摘要 三维(3D)无机微纳结构在光子学、量子信息、航空航天、能源等领域发挥着重要作用。利用传统制备方法获得的无机微结构通常分辨率较低和形貌不可控。因此,3D无机微纳结构的精确可控制备成为亟待解决的难题。激光加工具有高精度、形貌可控等优势,能够实现真3D、高分辨、多尺度复杂3D微纳结构的制备,解决3D无机微纳结构的精确可控制备难题。本文综述了激光加工制备无机微纳结构的研究进展,首先讨论了连续激光和超快脉冲激光加工方式,重点针对飞秒激光加工技术,阐述了基于纯无机材料体系、有机-无机杂化体系,以及聚合物模板法等制备3D无机微纳结构的方法。随后,总结了近年来激光加工3D无机微纳结构在光学器件、量子芯片、信息存储与防伪、航空航天以及仿生结构等领域的应用。最后,展望了激光加工3D无机微纳结构的未来发展趋势。

关键词 三维无机微纳结构；激光加工；飞秒激光；光与物质相互作用；微型器件

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China’s Top 10 Optical Breakthroughs: Laser Fabrication and Applications of 3D Inorganic Micro and Nanostructures (Invited)

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Abstract Three-dimensional (3D) inorganic micro and nanostructures play an important role in photonics, quantum information, aerospace, energy, and other fields. Inorganic microstructures prepared using traditional methods usually exhibit low resolution and uncontrollable morphology. The precise and controllable fabrication of 3D inorganic micro and nanostructures is a critical problem. Because of advantages such as 3D fabrication capability, high precision, and controllable morphology, laser fabrication can realize the preparation of 3D, high-resolution, and multiscale micro and nanostructures; furthermore, it can address the problem of accurate and controllable preparation of these 3D structures. In this study, the research progress of laser fabrication of inorganic micro and nanostructures was reviewed. First, continuous wave and ultrafast pulse laser fabrication methods were discussed, and especially, the femtosecond laser fabrication of 3D inorganic microstructures and nanostructures, including pure inorganic material systems, organic-inorganic hybrid systems, and polymer templates, were summarized. Further, the applications of 3D micro and nanostructures in optical devices, quantum chips, information storage, aerospace, and bionic structures in recent years were summarized. Finally, we highlighted the potential future development of the laser fabrication of 3D inorganic micro and nanostructures.

Key words three-dimensional inorganic micro and nanostructures; laser fabrication; femtosecond laser; light-matter interaction; micro devices

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‡ 本文为中国光学十大进展特邀综述。中国科学院理化技术研究所金峰、郑美玲联合暨南大学段宣明等，利用超快激光多光子效应，实现了无机光刻胶超衍射纳米光刻，为发展新型3D无机纳米结构和器件提供了新方法，相关成果获得了2022中国光学十大进展提名奖。详情请见“中国光学十大进展”官网。

1 引 言

无机材料具有优异的热稳定性和化学稳定性，较高的刚度和硬度，出色的光、电、磁学特性，在科研生产和日常生活中日益发挥重要作用。基于无机材料所制备的三维（3D）无机微纳结构具有小尺度、高精度等特点，能够适应高温、高压等极端环境。因此，3D 无机微纳结构在光学微器件[1-2]、光数据存储和信息加密[3-4]、量子芯片[5-6]、航空航天[7-8]、微流控系统[9-10]和仿生学[11-12]等领域有着广泛的应用前景。

3D 无机微纳结构的传统制备方法如化学刻蚀[13-14]、溶胶-凝胶法[15-16]、模板法[17-18]等，大多存在过程繁琐、复杂图案受限、精度较低、加工时间长等问题。因此，研究人员开发了一系列新的无机微结构加工技术：利用熔融沉积成型[19-20]制备机械性能良好的陶瓷，形成曲面、齿轮、牙齿等复杂结构；诱导自组装[21-22]析出晶体结构，产生特定形貌特征；通过墨水直写技术[23-25]，将特制纳米复合油墨从喷嘴挤出，打印出具有良好的光学性能和折射率梯度的无机平板光学微器件；使用数字光 3D 打印技术[26]加工出具有复杂 3D 形状的陶瓷刀具。这些微纳加工技术增强了对复杂微图案的设计加工能力，但尚难以精准构筑具有高精度和高分辨率的复杂 3D 无机微结构，仍无法满足各领域对 3D 无机微结构微型化、集成化和高性能化的新需求。

激光加工技术作为制备 3D 微纳结构的重要手段，能够实现真 3D、高分辨、多尺度 3D 微纳结构加工，包括连续激光加工技术和超快脉冲激光加工技术。连续激光加工技术是以连续激光作为光源，经过聚焦后作用于加工对象，属于“热加工”技术[27-28]。超快激光加工技术作为一种新兴技术手段，具有超短激光脉冲、超高能量密度的特点[29-31]，有望加工出具有复杂结构和高分辨率的 3D 无机微纳结构。由于与材料相互作用的时间极短，超快激光辐照区域的热效应几乎可以忽略不计，被认为是“冷加工”技术。超快激光加工技术可以通过加工纯无机材料、有机-无机杂化材料以及聚合物模板辅助等途径得到 3D 无机微纳结构。Liu 等[32]利用超快飞秒激光诱导化学键合，以超越衍射极限的分辨率直接打印出任意 3D 量子点结构，有望应用于制造自由形态的量子点光电器件。Bauer 等[33]采用有机-无机低聚倍半硅氧烷（POSS）光刻胶，利用飞秒激光结合高温烧结，形成 3D 高精度石英玻璃微纳结构和光子学器件。激光加工 3D 无机微纳结构无需掩模版、无污染、零接触、适合材料范围广，可以用来制备结构紧凑、尺寸小的集成化微结构，在光学器件[34]、微流控[35]、量子芯片[36]、仿生学[37-38]等领域有着广阔的前景。

本文介绍了激光加工 3D 无机微纳结构的研究进展与发展现状。首先简要概括了连续激光、皮秒激光加工制备的 3D 无机微结构，进一步详细讨论了基于纯无机材料体系、有机-无机杂化体系以及聚合物模板辅助等的飞秒激光加工 3D 无机微纳结构的研究现状。随后，本文总结了激光加工 3D 无机微纳结构在光学器件、量子芯片、信息存储与防伪、航空航天以及仿生学等领域的应用。最后，对激光加工 3D 无机微纳结构的未来发展趋势进行了展望。

2 3D 无机微纳结构的激光加工技术

激光加工技术具有高精度、非接触、可控性强、材料适应性广等特点，通过光与物质相互作用，实现对材料的切割、打孔、雕刻和微结构加工等。激光加工技术按照使用的光源类型可分为连续激光加工技术和脉冲激光加工技术，其中脉冲激光加工技术主要基于皮秒激光和飞秒激光。激光加工技术具有高分辨、低成本的优势，成为构筑 3D 无机微结构的重要途径。近年来，激光加工制备的各种 3D 无机微结构已经广泛应用于国防建设和生命健康等领域。

2.1 连续激光加工 3D 无机微纳结构

连续激光加工 3D 无机微结构是无机材料通过吸收激光能量，发生各种物理化学效应，从而形成所需的 3D 无机微结构。Hu 等[3]发现在 473 nm 半导体激光照射下，稀土离子掺杂的磷酸钨玻璃产生可逆的发光调制，颜色由浅黄色变为蓝色，实现了信息数据在透明玻璃内的任意写入与擦除[图 1(a)]。Liu 等[39-40]利用二氧化碳（CO_2）激光加热直径为 196 μm 的熔融石英玻璃丝，实现熔融石英层与层之间的键合，制备了 105 层的 3D 玻璃结构和高质量的微透镜阵列[图 1(b)、(c)]。Toombs 等[41]利用 442 nm 激光对掺杂二氧化硅（SiO_2）纳米粒子的光刻胶进行立体光固化得到有机-无机 3D 微结构，随后高温烧结去除有机成分，制备出内径为 150 μm 的 3D 微流体通道及最小特征尺寸为 50 μm 的复杂高强度桁架和点阵结构[图 1(d)]。Zhao 等[42]利用 980 nm 近红外连续激光作为光源，通过喷墨打印陶瓷浆料结合光固化形成稳定自支撑结构，打印出多尺度扭转弹簧、3D 弯曲、悬梁臂等 3D 陶瓷微结构，为无支撑 3D 陶瓷微结构和器件的构筑与应用提供了新思路[图 1(e)]。连续激光加工技术虽然能够稳定灵活地在多种材料表面或内部制备出 3D 无机微纳结构，但其加工的精度低，且存在热效应，难以满足高精度 3D 无机微纳结构的制备需求。

2.2 皮秒激光加工 3D 无机微纳结构

皮秒激光加工技术由于高峰值功率密度能够实现 3D 微纳结构的加工。皮秒脉冲激光与材料作用时间短，有效地降低了连续激光加工中的热效应，能够以较低的热影响实现复杂 3D 微纳结构的加工。皮秒激光加工技术在无机微纳结构加工中具有独特的优势和应用潜力，可以实现高断裂强度的区域焊接[43]。Penilla 等[44]利用皮秒激光脉冲照射，在室温条件下将具有复杂形状的陶瓷微结构进行焊接，有望应用于温度敏感的微机械系统等领域[图 2(a)]。其次，皮秒激光还可

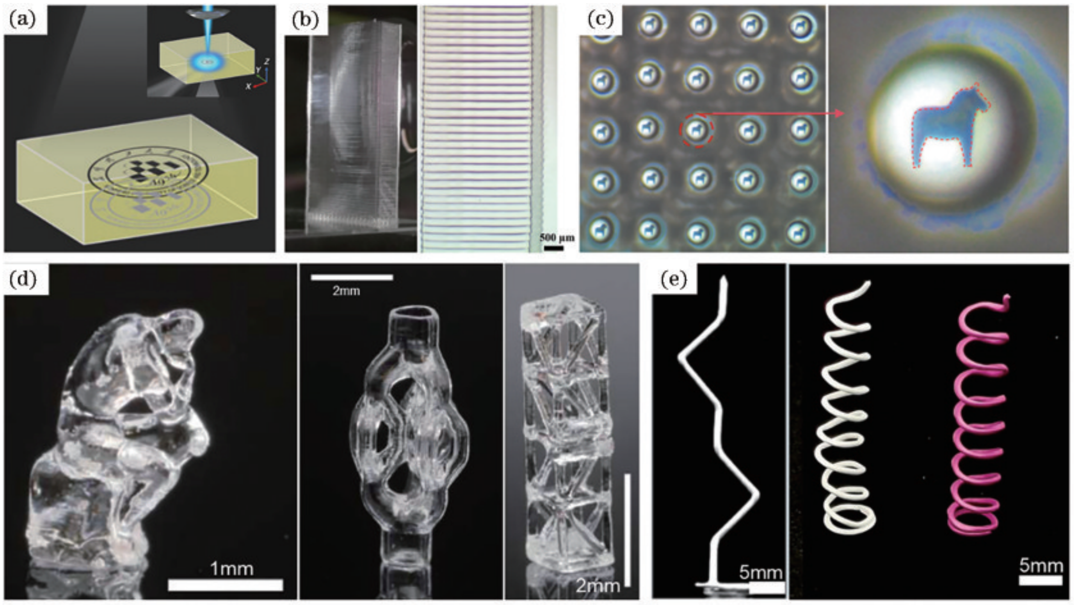

图 1　连续激光加工 3D 无机微纳结构。(a) 473 nm 连续激光在玻璃内写入图案信息[3]；(b) CO_2激光加工的 105 层 3D 玻璃结构的实物照片(左)和侧壁截面的光学显微镜图像(右)[39]；(c) CO_2激光加工的玻璃微透镜阵列，右图是单个微透镜成像效果图[40]；(d) 442 nm 连续激光加工的 3D 透明玻璃微结构[41]；(e) 980 nm 连续激光打印的 3D 无支撑陶瓷微结构[42]

Fig. 1　Continuous wave (CW) laser fabrication of 3D inorganic micro and nanostructures. (a) 473 nm CW laser writes patterning information in glass [3]; (b) photograph of 105 layers glass structure processed by CO_2 laser (left), optical microscope image of sidewall section (right)[39]; (c) glass microlens array processed by CO_2 laser, the image on the right is the image effect of a single microlen[40]; (d) 3D transparent glass microstructures processed by 442 nm CW laser[41]; (e) unsupported ceramic microstructures fabricated by 980 nm CW laser [42]

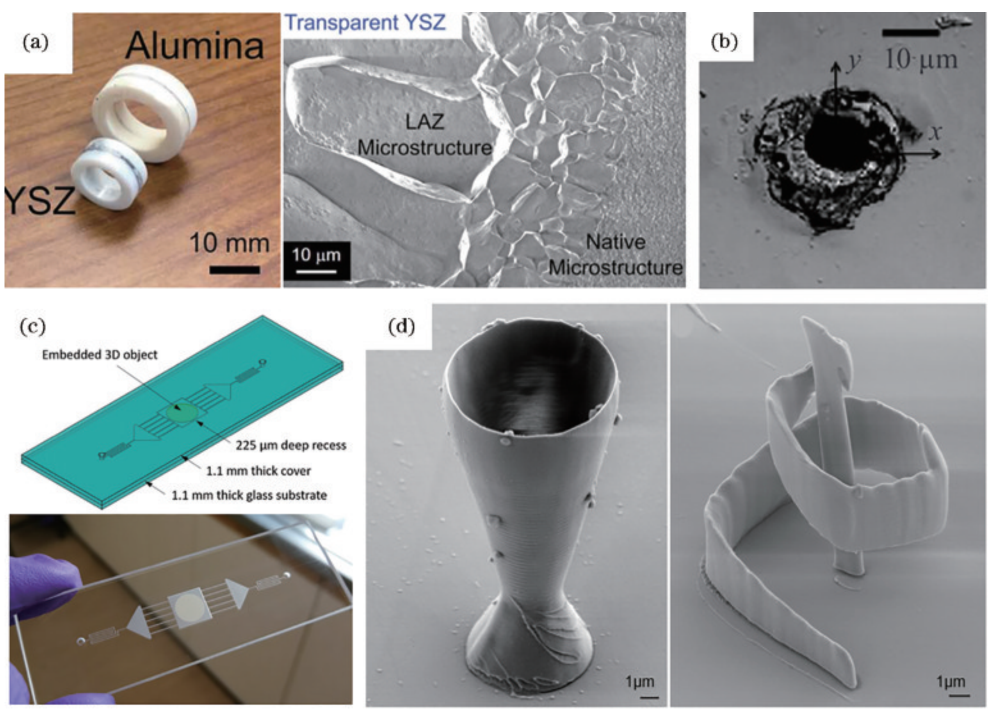

图 2　皮秒激光加工 3D 无机微纳结构。(a)皮秒激光焊接陶瓷组件[44]；(b)损伤通道端面图[46]；(c)皮秒激光在透明玻璃内嵌入 3D 结构[47]；(d)皮秒激光加工 HSQ 得到玻璃 3D 微结构[51]

Fig. 2　Picosecond laser fabricating 3D inorganic micro and nanostructures. (a) Picosecond laser welding ceramic components[44]; (b) end face of damaged channel[46]; (c) picosecond laser embedded 3D structure in transparent glass[47]; (d) 3D microstructure of glass fabricated by picosecond laser fabricating HSQ[51]

用于直写材料表面或内部的微流控通道[45-47][图 2(b)]。Wlodarczyk 等[47]利用皮秒脉冲激光在透明玻璃基底实现了微流控的快速加工[图 2(c)]。皮秒激光还可用于制备微孔结构[48]和多级粗糙结构[49]。Nguyen 等[50]利用皮秒激光在无机玻璃上加工出各种微纳分级结构，如西兰花状和锥形微结构等，实现超疏水性能。此外，利用激光脉冲照射无机光刻胶氢倍半硅氧烷(HSQ)，HSQ 发生交联反应产生 3D 结构，经加热后得到光学性能、机械性能优异的 3D 石英玻璃微纳结构[51][图 2(d)]。

2.3　飞秒激光加工 3D 无机微纳结构

飞秒激光作为一种“冷加工”技术[52-53]，已经成为精密加工领域的重要手段，可以制备出高精度、复杂 3D 微结构。飞秒激光加工 3D 无机微纳结构按照所使用材料的不同，大致可以分成三类。第一类是使用飞秒激光直接加工纯无机材料如玻璃、光学晶体、陶瓷和量子点等形成 3D 无机微纳结构。第二类是利用飞秒激光加工有机-无机杂化材料先形成复杂 3D 微纳结构，然后经过热处理去除有机成分，形成致密的、光学性质和机械性能优良的 3D 无机微纳结构。有机-无机杂化材料又分为可转化为无机材料的光刻胶前驱体，以及无机纳米颗粒掺杂有机光刻胶两种材料体系。第三类是通过聚合物模板法辅助制备 3D 无机微纳结构，即通过飞秒激光加工先制备出聚合物模板，再利用沉积、溅射等手段将无机材料涂覆在表面，最后经过热处理、等离子体刻蚀、特定溶液降解等去除聚合物得到 3D 无机微纳结构。

2.3.1　飞秒激光加工纯无机材料制备 3D 无机微纳结构

玻璃具有优良的透光性、化学稳定性、生物相容性、机械强度等，玻璃微纳结构在集成光子学和量子芯片等领域中具有极大的应用价值。1996 年，Davis 等[54]首次利用 810 nm 飞秒激光在块体玻璃内部留下微纳线条结构，证明飞秒激光可在玻璃内部书写光波导结构[图 3(a)]。De Aldana 等[55]利用飞秒激光加工 Er^{3+}/Yb^{3+}离子共掺的透明氟氧化物纳米玻璃陶瓷，实现了平面和 3D 光波导，拓宽了在集成有源光子器件领域的应用。针对飞秒激光在玻璃中直写的波导结构弯

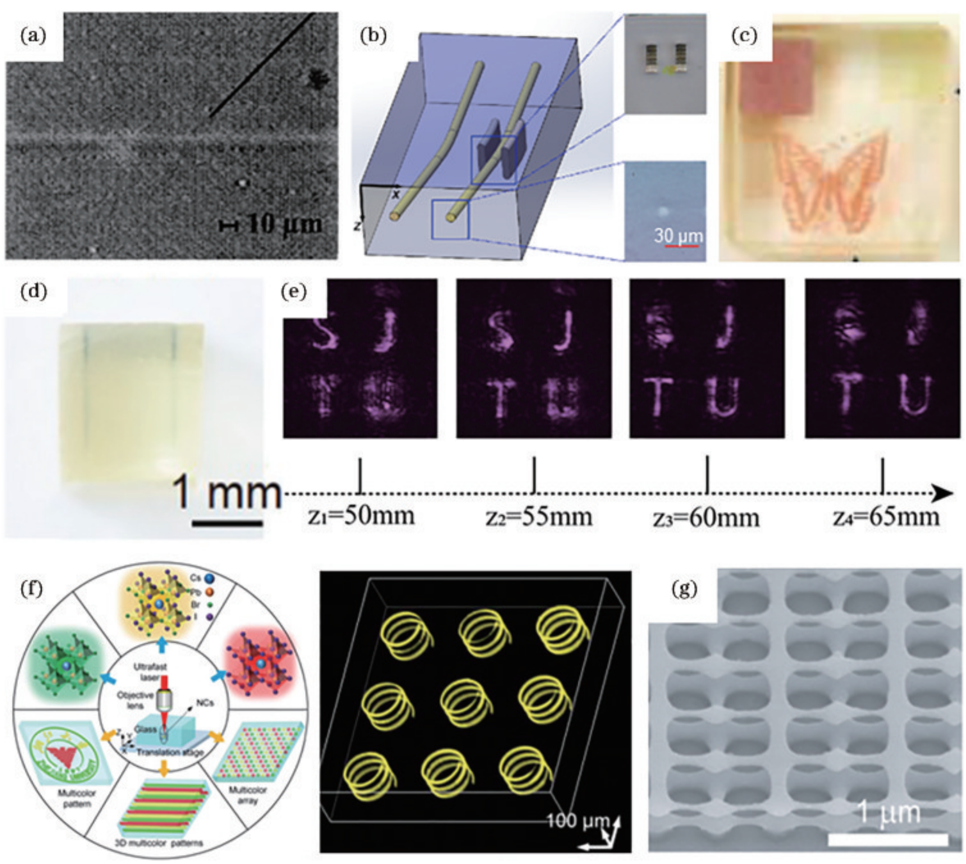

图 3　飞秒激光加工玻璃基质的 3D 无机微纳结构。(a)飞秒激光在玻璃内写入永久痕迹[54]；(b)飞秒激光在玻璃内写入低损耗的弯曲波导[56]；(c)飞秒激光在掺 Au 玻璃内部的图案化[62]；(d)飞秒激光在玻璃内写入包含深度信息的图像[64]；(e)飞秒激光在玻璃中制备 3D $CsPbBr_3$纳米晶体结构[65]；(f)飞秒激光在 HSQ 上加工 3D 无机微结构[69]

Fig. 3　Femtosecond laser fabrication of 3D inorganic micro and nanostructures in glass. (a) Permanent trace in glass[54]; (b) femtosecond laser writes low loss curved waveguide in glass[56]; (c) patterning of femtosecond laser inside Au doped glass[62]; (d) femtosecond laser writing of depth information in glass[64]; (e) $CsPbBr_3$ nanocrystalline structures prepared by femtosecond laser[65]; (f) femtosecond laser writing 3D inorganic microstructure based on HSQ[69]

曲损耗问题，Liu 等[56]通过将弯曲波导夹在飞秒激光写入玻璃内时产生的垂直壁之间，加速区域折射率的变化，将损耗减小至 0.3 dB[图 3(b)]。飞秒激光加工技术还能在玻璃表面和内部写入各种波导和微通道等[57-61]。Qiu 等[62]利用飞秒激光照射诱导玻璃内部使得金纳米颗粒选择性析出[图 3(c)]。Li 等[63]利用近红外飞秒激光脉冲在石英玻璃内部制备光栅等折射率型元器件，并通过钻孔引入蒸馏水，在钠钙玻璃中加工出纵横比较大的微细直孔，制备了直线型和波浪型等不同形状的线条。玻璃优良的光学性能不仅可以制备特定的光传递通道，还能够可逆存储数据，实现在信息加密和防伪领域的应用[64][图 3(d)]。Sun 等[65]提出通过超快激光诱导纳米相分离，从而实现内部成分可调的钙钛矿纳米晶体，所制备的 3D 图案化纳米晶在全彩印刷、光存储、微型发光以及全息成像等领域展现很好的应用前景[图 3(e)]。飞秒激光在玻璃中形成发光钙钛矿纳米晶在防伪编码、微结构图案化等方面也具有潜在的应用价值[66-68]。2022 年，Jin 等[69]利用飞秒激光多光子加工技术，在 HSQ 光刻胶中实现了仅为激光波长 1/30 的 26 nm 特征尺寸 SiO_2 结构的直写，大大超越光学衍射极限。利用该技术制备了多种具有优异的耐高温和耐溶剂特性的 3D 无机微结构与器件，为应用于极端环境的功能微纳器件的制备拓宽了思路[图 3(f)]。

光学晶体具有较大的非线性光学系数、稳定的理化性质和良好的机械强度，被用于制备光波导、光调制器等光子学器件。研究人员利用飞秒激光加工技术在钇铝石榴石（YAG：Nd^{3+}）晶体[70]、硫化锌（ZnS）晶体[71]、掺铥氟化钇锂（Tm：YLF）晶体[72]、三硼酸锂（LBO）晶体[73]、铌酸锂晶体（$LiNbO_3$）[74]、钛蓝宝石（Ti：sapphire）晶体[75]和蓝宝石（sapphire）晶体[76]中制备了预定形状的波导结构[图 4(a)～(d)]，降低传输过程的损耗。$LiNbO_3$ 晶体具有光电效应和性能可调控性，研究人员利用飞秒激光在 $LiNbO_3$ 晶体中进行纳米级分辨率的可重构 3D 铁电畴工程，在高效混频、高频声谐振器和高容量非挥发性铁电体中具有重大应用前景[77-78][图 4(e)]。2023 年，Wu 等[79]通过飞秒激光在 $LiNbO_3$ 中实现了可切换弯曲方向的非线性艾里光束，在光捕获、光通信和生物医学成像等领域具有广泛的应用前景。Zhu 等[80]利用飞秒激光微加工制备二进制计算机全息图，在单块 $LiNbO_3$ 晶体加工特定图案实现二次谐波全息成像[图 4(f)]。

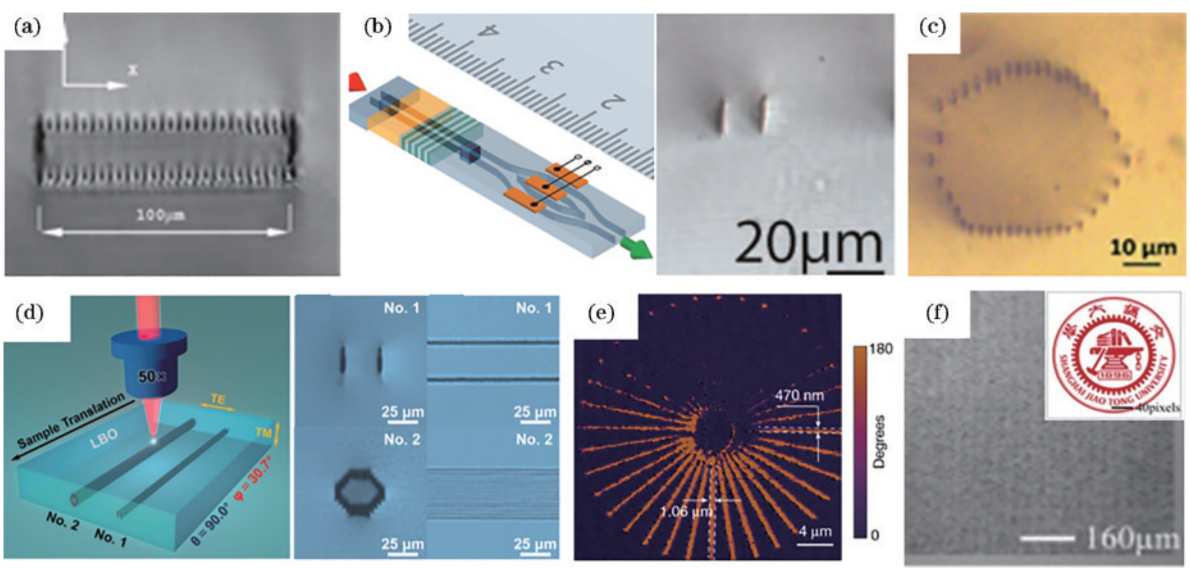

图 4　飞秒激光在光学晶体中加工 3D 无机微纳结构。(a) YAG：Nd^{3+} 中刻写的凹陷包层波导的端视图[70]；(b) $LiNbO_3$ 晶体中写入波导端面图[74]；(c) ZnS 晶体中波导的截面[71]；(d) LBO 晶体中产生的双线（No. 1）和凹陷包层（No. 2）波导[73]；(e)飞秒激光在 $LiNbO_3$ 晶体中的纳米级调控[78]；(f)飞秒激光在 $LiNbO_3$ 晶体中写入特定图案的全息图像[80]

Fig. 4　Femtosecond laser fabricating 3D inorganic micro and nanostructures in optical crystal. (a) End view of concave cladding waveguide written in YAG : Nd^{3+} [70]; (b) waveguide end face written in $LiNbO_3$ crystal[74]; (c) cross section of waveguide in ZnS crystal[71]; (d) double line (No. 1) and concave cladding (No. 2) waveguides generated in LBO crystal[73]; (e) nanoscale regulation of femtosecond laser in $LiNbO_3$ crystal[78]; (f) femtosecond laser writes holograms of specific patterns in $LiNbO_3$ crystal[80]

量子点因其优异的光学性能和尺寸调控特性，而被广泛应用于微纳发光器件和显示等领域。Liu 等[32]提出光激发诱导化学键合，利用飞秒激光照射半导体量子点激发出的空穴转移到纳米晶体表面，从而诱导粒子间的化学键合，打印出高精细 3D 量子点结构[图 5(a)]。Li 等[81]将双叠氮分子与纳米晶体溶液混合，利用飞秒激光照射引发颗粒间的交联反应，采用 CdSe/ZnS 核壳量子点打印出洋红色 3D 纳米柱阵列“龙”图案[图 5(b)]。2023 年，Liang 等[82]利用飞秒激光诱导钙钛矿量子点正向转移，将薄膜上的钙钛矿量

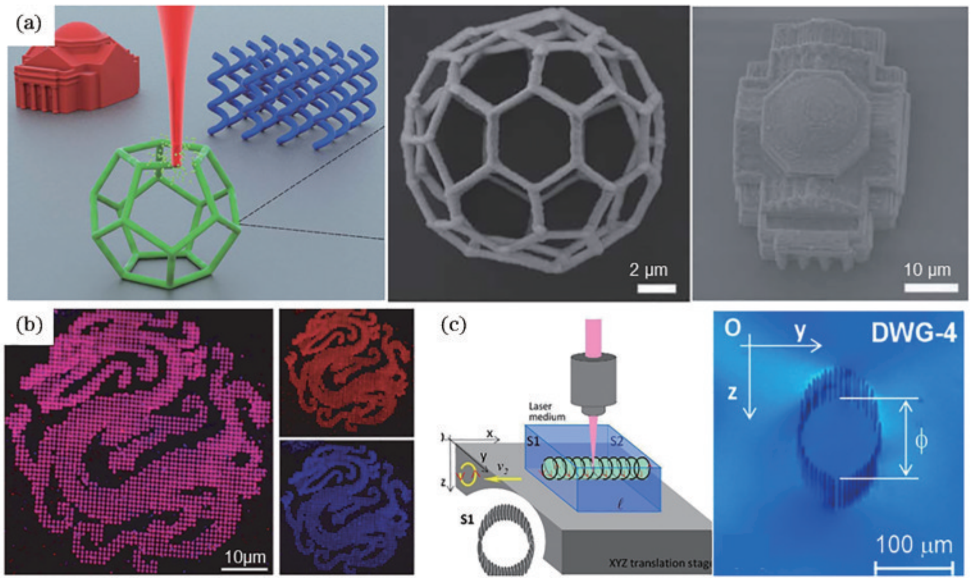

图 5　飞秒激光加工 3D 量子点、陶瓷微结构。(a)飞秒激光诱导量子点化学键合形成 3D 无机微纳结构[32]；(b)飞秒激光打印混合量子点形成 3D 纳米柱阵列[81]；(c)飞秒激光在陶瓷中以螺旋式运动加工圆形波导[84]

Fig. 5　Femtosecond laser fabrication of 3D inorganic micro and nanostructures based on ceramics and quantum dots. (a) Femtosecond laser-induced chemical bonding of quantum dots to form 3D inorganic micro and nanostructures[32]; (b) femtosecond laser printing of mixed quantum dots to form a 3D nanopillar array[81]; (c) femtosecond laser fabricating circular waveguides in ceramics with spiral motion[84]

子点转移到衬底上，制备出分辨率达 2 μm 的阵列，在高分辨率的全彩显示和信息加密防伪领域具有潜在的应用前景。

陶瓷材料因其硬度大、脆性大、耐高温、耐磨损、耐腐蚀的优势，广泛用于航空航天、电子器件、生物医药等领域。但其较大的刚硬度和较差的透明度，导致传统加工方式难以制造出 3D 异形结构。而利用飞秒激光加工技术，无需掩模版就能够高精度地加工复杂陶瓷微结构。Castillo-Vega 等[83]对光学透明氧化钇稳定氧化锆(YSZ)陶瓷进行激光加工，辐照区域光学性质发生永久性变化。随后沿螺旋轨迹写入激光，成功制备出圆形波导[84][图 5(c)]。

2.3.2　飞秒激光加工有机-无机前驱体光刻胶制备 3D 无机微纳结构

飞秒激光加工有机-无机前驱体光刻胶能够制备出 3D 无机微结构。首先，利用飞秒激光加工出前驱体光刻胶微纳结构，再经过高温处理等去除有机成分，得到 3D 无机微纳结构[85][图 6(a)]。Yee 等[86]利用飞秒激光直写含有金属离子的光固化树脂，制备出特征尺寸为 250 nm 的氧化锌 3D 微结构[图 6(b)]。Gailevičius 等[87]利用飞秒激光在光刻胶 SZ2080 中制备出几百纳米的 3D 结构，随后烧结去除有机物成分，形成陶瓷 3D 微结构[图 6(c)]。由于有机-无机前驱体光刻胶中有机物的含量较高，高温热处理会引起结构较大的收缩，甚至会导致 3D 图案的扭曲和分层[88-89][图 6(d)、(e)]。为了减小热后处理过程中产生的收缩，Park 等[90]利用双功能无机聚合物烯丙基氢化聚碳硅烷(AHPCS)和有机金属(Z5-环戊二烯基甲基)-三甲基铂($CpPtMe_3$)作为添加剂，从光敏前驱体中制备了具有优异的尺寸稳定性和本征机械强度的近零收缩的碳化硅陶瓷微结构[图 6(f)]。Hong 等[91]开发了一种无溶剂、甲基丙烯酰氧基改性的 SiO_2 前驱体，先制备出微透镜和光栅等结构，然后在 600 ℃的温度下完全转化为透明的玻璃结构，收缩率为 17%，表面粗糙度低于 6 nm[图 6(g)]。2023 年，Bauer 等[33]提出了一种中等温度烧结的飞秒激光加工复杂三维熔融石英玻璃纳米结构，成功制备出特征尺寸 97 nm 的熔融石英微结构。这项研究通过飞秒激光加工有机-无机 POSS 杂化光刻胶，加工出高质量的 3D 结构，随后经过 650 ℃的热处理将该结构转化为熔融石英玻璃 3D 微结构，大大降低了后期热处理的温度，为熔融石英玻璃 3D 微纳结构的制备提供了新途径[图 6(h)]。

2.3.3　飞秒激光加工无机纳米颗粒掺杂光刻胶体系制备 3D 无机微纳结构

通过将无机纳米颗粒掺杂到有机光刻胶中，利用飞秒激光加工结合高温烧结，即“掺杂-加工-烧结”工序，可实现 3D 无机微纳结构的制备。Kotz 等[92]利用飞秒激光直写含 SiO_2 纳米颗粒的光刻胶，制备了具有几十微米分辨率和表面粗糙度约为 6 nm 的 3D 熔融石英玻璃，该结构在 780 nm 波长处显现出 91.6% 的高透明度[图 7(a)]。Desponds 等[93]将 45% 氧化锆纳米颗粒掺入丙烯酸锆前驱体中，通过控制纳米粒子的尺寸，利用飞秒激光 3D 微加工和进一步热处理，成功制备出周期为 0.8 μm 的微透镜阵列[图 7(b)]。2021 年，

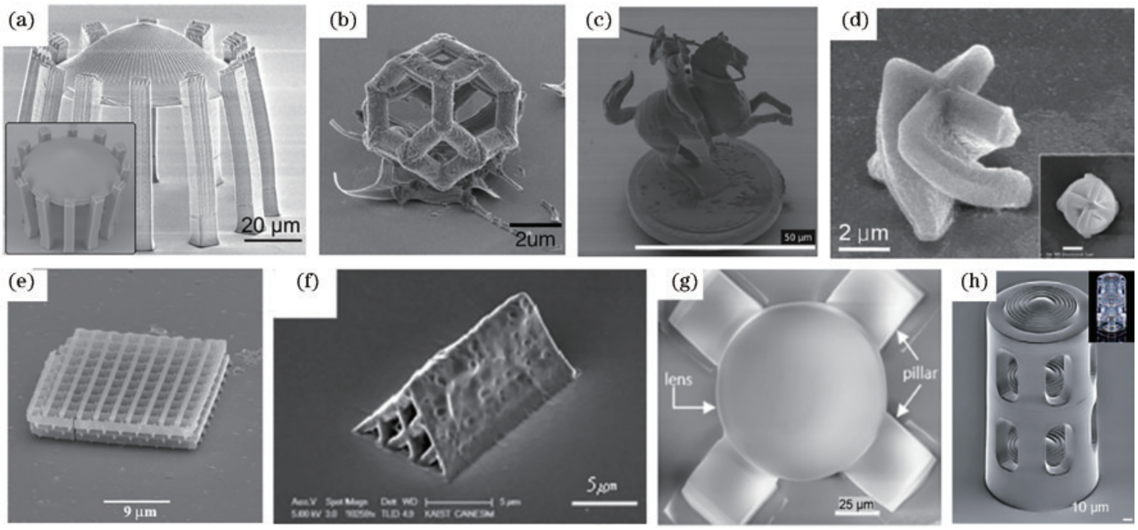

图 6 飞秒激光在含无机组分的前驱体光刻胶中加工 3D 无机微纳结构。(a)自支撑非球面微透镜[85];(b)十四面体晶胞[86];(c)自由形态雕塑[87];(d)微米十字扭转结构[88];(e)干燥收缩过程引起 3D 结构裂纹[89];(f)多孔微通道结构[90];(g)印刷在支撑柱上的微透镜[91];(h)150 μm 高的多透镜衍射微物镜[33]

Fig. 6 Femtosecond laser fabricating of 3D inorganic micro and nanostructures in precursor photoresist containing inorganic components. (a) Self supporting aspheric microlens[85]; (b) tetrahedral cell[86]; (c) free form sculpture[87]; (d) micron cross torsion structure[88]; (e) drying shrinkage process causes 3D structural cracks[89]; (f) porous microchannel structure[90]; (g) microlens printed on support column[91]; (h) 150 μm-high diffractive micro objective lens[33]

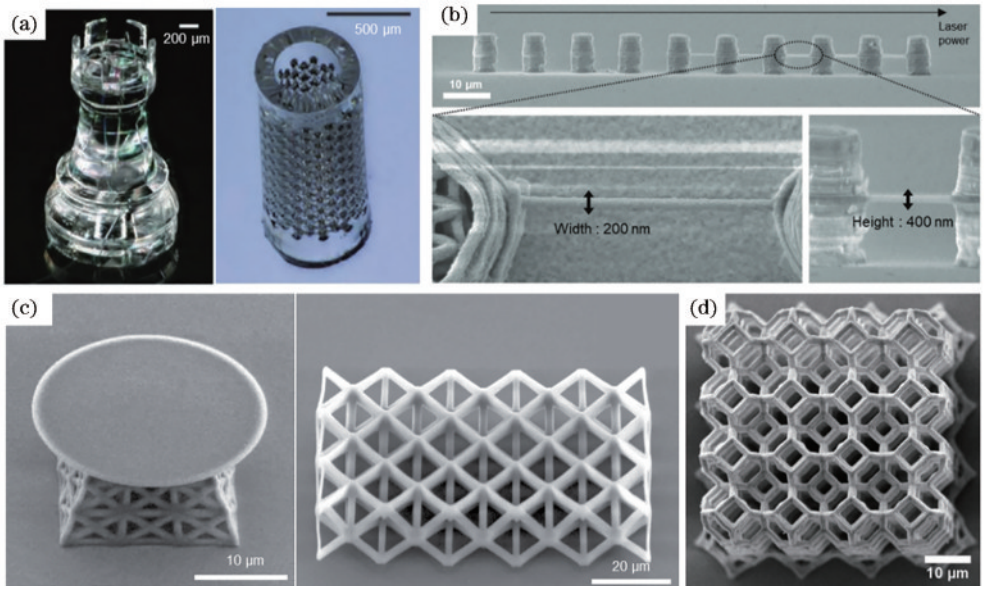

图 7 飞秒激光加工无机纳米粒子掺杂的光刻胶制备 3D 无机微纳结构。(a)透明玻璃微结构[92];(b)悬垂线[93];(c)玻璃圆盘桁架结构(左)和八面体桁架结构(右)[94];(d)陶瓷点阵立方体[95]

Fig. 7 Femtosecond laser fabrication of 3D inorganic micro and nanostructures based on inorganic nanoparticles doped photoresists. (a) Transparent glass microstructure[92]; (b) pendant[93]; (c) disk truss structure (left) and octahedral truss structure (right)[94]; (d) ceramic lattice cube[95]

Wen 等[94]将功能化的 SiO_2 纳米粒子掺杂到光刻胶中，利用飞秒激光加工和后烧结工艺加工出具有 200 nm 分辨率的高质量复杂 3D SiO_2 微结构[图 7(c)]，在构建高品质因子值的微环谐振器和集成 SiO_2 微光子芯片方面展现出较大的潜力。Sänger 等[95]利用高达 80% 负载量的 YSZ 透明陶瓷浆料，通过飞秒激光加工技术制备出复杂的 3D 陶瓷微结构，分辨率达到了 500 nm，经高温烧结后得到抗压强度与纯 YSZ 相当的致密陶瓷结构[图 7(d)]。

2.3.4 聚合物模板法辅助制备 3D 无机微纳结构

飞秒激光加工技术还可以通过聚合物模板法辅助加工 3D 无机微纳结构。首先，利用飞秒激光加工出 3D 聚合物微结构作为模板，随后通过沉积、溅射等将无机材料涂覆在聚合物模板表面，经热处理、等离

子体刻蚀、特定溶液降解等去除模板获得3D无机微纳结构。Meza等[96-97]采用飞秒激光加工3D支架结构，通过原子层沉积在支架上沉积一层氧化铝薄膜，利用聚焦离子束打磨最外层和氧等离子体刻蚀技术制备了空心管状氧化铝纳米点阵[图8(a)]。Kotz等[10]则提出飞秒激光加工DNA双螺旋结构和微流控通道模板，再将聚合物模板嵌入纳米复合材料中，经光照射后纳米复合材料聚合，随后热处理去除聚合物形成复杂中空微玻璃结构[图8(b)]。Xia等[98]通过飞秒激光加工出周期性3D四方微点阵，并在点阵上溅射一层厚度约为100 nm的Ni层，随后在Ni膜上沉积约300 nm的非晶态Si层，制备出高度均匀的聚合物/Ni/Si杂化结构[图8(c)]。2021年，Diamantopoulou等[99]提出刚度和形状恢复性较好的双壁陶瓷纳米晶格[图8(d)]。2022年，Liu等[100]提出了一种飞秒激光加工牺牲模板的方法，制备了含纳米颗粒有序排列的复杂无机3D微结构，最小特征尺寸可达到3 μm[图8(e)]。

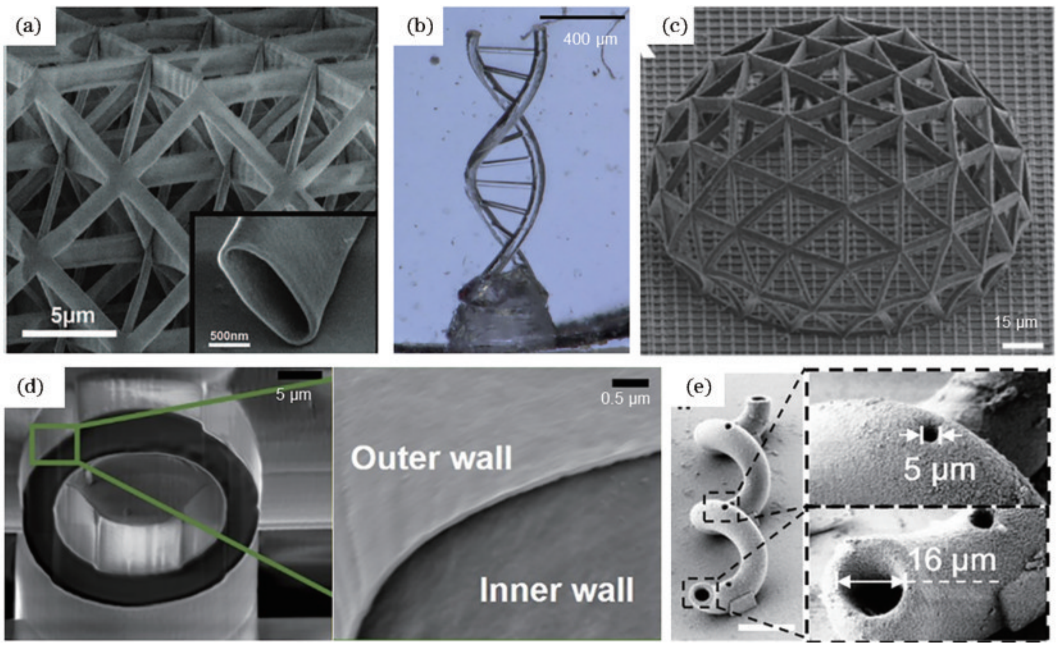

图8 聚合物模板法辅助飞秒激光加工制备3D无机微纳结构。(a)氧化铝八面体桁架纳米晶格[97]；(b)DNA双螺旋中空玻璃微结构[10]；(c) 3D硅纳米结构[98]；(d)双壁陶瓷纳米晶格[99]；(e) 3D中空螺旋微管结构[100]

Fig. 8 3D inorganic micro and nanostructures prepared by the polymer template assisted femtosecond laser fabrication method. (a) Alumina octahedral truss nanolattice[97]; (b) microstructure of DNA double helix hollow glass[10]; (c) 3D silicon nanostructure[98]; (d) double-well ceramic nanolattice[99]; (e) 3D hollow spiral microtubule structure[100]

3 应 用

激光加工技术无接触、无污染、加工速度快、精度高，是制备3D无机微纳结构的重要手段。与传统加工技术相比，激光加工技术更能满足新型功能器件微型化、集成化的发展需求，制备出形状尺寸可控的复杂3D无机微纳结构，在微型光子学器件、量子技术、信息存储与加密、航空航天以及仿生结构等领域有着广泛的应用。

3.1 光学器件

激光加工技术制备的3D无机微纳结构广泛应用于构筑微型光学器件，如集成光子学的基本元件回音壁微谐振腔、自由曲面透镜等。Fang等[101]利用飞秒激光在$LiNbO_3$中制备了品质因子高达10^7的回音壁微谐振腔。Wen等[94]基于SiO_2纳米复合材料打印出高品质因子的微环回音壁谐振腔[图9(a)]。Kotz等[92]对SiO_2纳米复合材料进行飞秒激光直写，制备出透明的光学微透镜，成功对细胞结构进行显微成像[图9(b)]。Hong等[2]提出了具有高固化速度的新型液体石英树脂，利用飞秒激光加工后低温烧结，实现表面粗糙度低于5 nm的高精度自由曲面玻璃光学器件，同时成功制备出具有多个光学元件和主动运动元件的复杂光学系统，为微光学系统提供了新途径[图9(c)]。Jin等[69]利用飞秒激光直写HSQ，构筑的光学微器件菲涅耳透镜具有良好的耐热性能和耐溶剂性能，为飞秒激光制备耐极端环境的微型无机光学微器件提供了新方法[图9(d)]。2023年，Huang等[51]利用HSQ制备出亚微米分辨率的光子微型环芯谐振器与总线波导[图9(e)]。Bauer等[33]利用飞秒激光加工结合650 ℃后热处理制备出熔融石英玻璃自由曲面微光学器件，展示了出色的光学性能[图9(f)]。激光加工技术的高效率、高精度为微型化、集成化和可设计的微光学器件的制备奠定了坚实的基础。

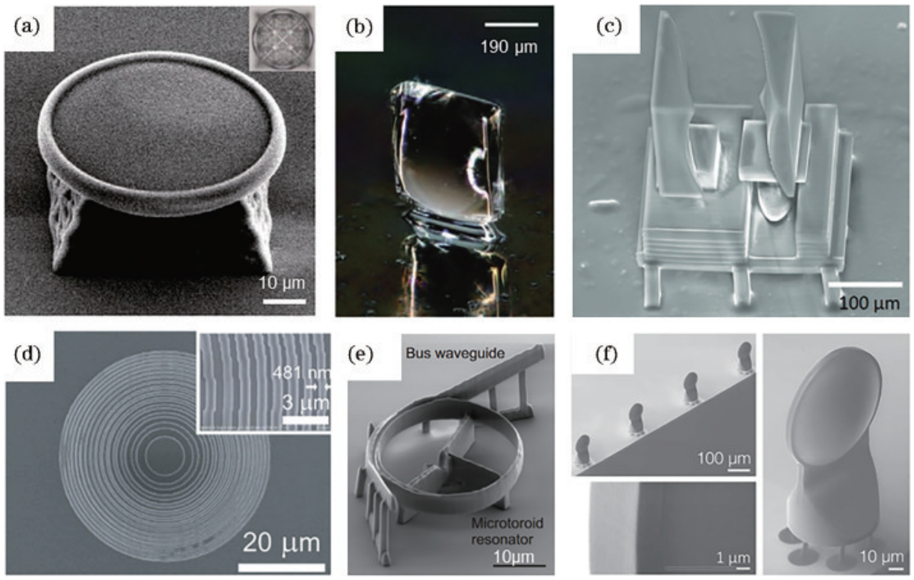

图 9 3D 无机微结构在光学微器件中的应用。(a)微环光学谐振腔[94];(b)玻璃微透镜[92];(c) Alvarez 透镜[2];(d)菲涅耳透镜[69];(e)光子微型环芯谐振器[51];(f)非球面轮廓的平凸微透镜[33]

Fig. 9 Application of 3D inorganic microstructure as optical micro devices. (a) Microring optical resonator[94]; (b) glass microlens[92]; (c) Alvarez lens[2]; (d) Fresnel lens[69]; (e) photonic micro ring resonator[51]; (f) plano convex microlens with aspheric profile[33]

3.2 量子芯片

量子芯片作为量子计算机的核心，是目前各国竞相追逐的科学前沿。利用飞秒激光在玻璃、铌酸锂等无机材料中加工微型波导等结构，是构筑量子芯片的重要途径。Flamini 等[102]利用飞秒激光在玻璃中写入动态可重构的集成光子电路，实现了对单光子态和双光子态的调控，条纹可见度大于 95%，为可重构光量子电路开辟了道路[图 10(a)]。飞秒激光不仅能写入

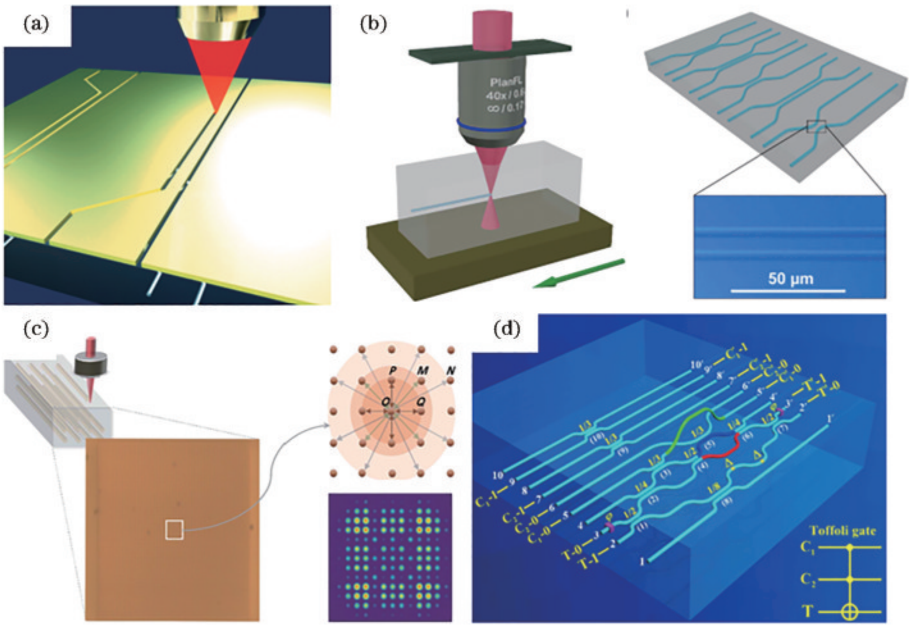

图 10 激光加工 3D 无机微纳结构应用于量子芯片。(a)飞秒激光图案化加工电阻器[102];(b)飞秒激光在玻璃内部直写光波导(左)和波导定向耦合器(右)[104];(c)飞秒激光直写 3D 波导阵列(左上)，光子晶格截面图(左下)，3D 波导阵列中一个波导耦合到其他波导的示意图(右上)，单光子在晶格中量子行走后输出的演化图案(右下)[106];(d)飞秒激光直写路径编码三量子比特 Toffoli 门[107]

Fig. 10 Laser fabrication of 3D inorganic micro and nanostructures for quantum chips. (a) Femtosecond laser patterns resistors[102]; (b) femtosecond laser directly writing optical waveguide (left) and waveguide directional coupler (right) inside the glass[104]; (c) femtosecond laser direct writing 3D waveguide array (top left), photonic lattice section (bottom left), schematic diagram of coupling one waveguide to other waveguides in a 3D waveguide array (upper right), and evolution pattern of single photon output after quantum walk in the lattice (lower right)[106]; (d) 3D layout of three qubit Toffoli gate encoded by femtosecond laser direct writing path[107]

光波导处理偏振编码量子位[103]，还能加工波导定向耦合器等其他元件，如Marshall等[104]利用飞秒激光在熔融石英玻璃中制备出量子芯片中重要的定向耦合器[图10(b)]。无论是在量子计算领域，还是在量子模拟领域，光量子芯片在信息处理上均展示了强大的功能[105]。Tang等[106]使用飞秒激光直写二维波导阵列实现连续量子行走，制备了节点数为49×49，多达2401个节点的光量子计算芯片[图10(c)]。Li等[6]利用飞秒激光直写技术在玻璃中制备出由Hadamard和可控非门(CNOT)组成的集成光量子芯片，产生了四个路径编码的贝尔纠缠态，可应用于各种高质量高保真度的光量子集成芯片。2022年，Li等[107]设计并展示了基于飞秒激光制备技术的路径编码光量子Toffoli门芯片，将二维量子线路优化为更简洁的3D立交桥状波导，消除了与其他波导间的交叉和耦合，大大提升了量子芯片的性能[图10(d)]。2023年，Skryabin等[108]利用飞秒激光构筑了一个低损耗的可重构光子芯片，实现了单量子比特和两量子比特操作。飞秒激光加工量子芯片的方法能够将3D路径和偏振等自由度结合，进一步简化量子线路，降低损耗，从而实现更复杂、更强大的3D光量子芯片的制备。

3.3　信息存储与加密

3D无机微纳结构存储信息具有长期稳定性和多样性，通过设计和组装能够大大提高存储容量和存储稳定性。1996年，Glezer等[109]利用飞秒激光脉冲聚焦在透明材料内部，产生较大折射率的亚微米比特，可用于永久性的3D光学数据存储。Smetanina等[110]利用飞秒激光脉冲在掺银磷酸盐玻璃中诱导形成局域二次和三次谐波，实现非线性光数据存储。在3D无机微纳结构中结合量子点的荧光特性，通过光学防伪进一步保障信息存储的安全性。2020年，Huang等[66]利用飞秒激光在玻璃中形成蓝光钙钛矿纳米晶，可以在玻璃中写入3D图案，该荧光图案在激光的照射下，可以局部擦除后恢复，为信息存储安全、防伪编码提供了应用价值[67][图11(a)、(b)]。Sun等[65]利用飞秒激光直接在玻璃内诱导钙钛矿纳米晶，产生多色的发光图案，增强了防伪效果[图11(c)]。2023年Liang等[82]实现了高分辨全彩的钙钛矿量子点阵列和任意微图案的制备，在荧光防伪领域具有广阔的应用前景。

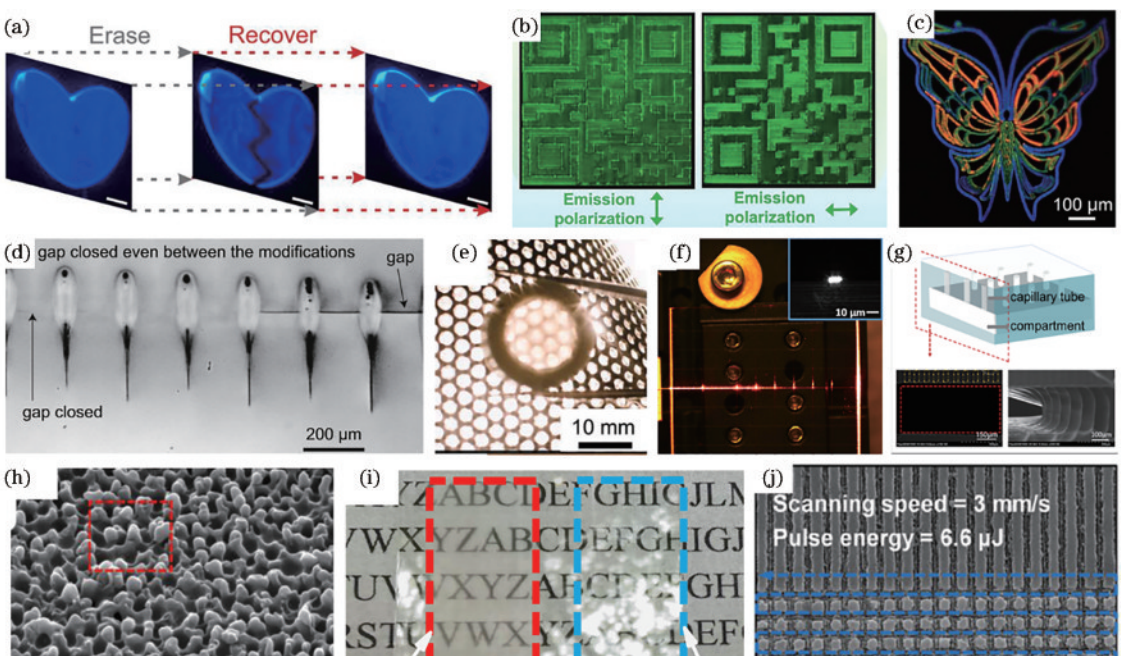

图11　激光加工3D无机微纳结构的应用。(a)飞秒激光擦除/恢复过程[66]；(b) QR码加密演示[67]；(c) $Cl^-Br^-—I^-$共掺杂玻璃图案化[65]；(d)激光焊接侧面图[112]；(e)激光焊接成功的装配图[44]；(f)传感器内的垂直波导[7]；(g)储仓微结构[115]；(h)圆偏振激光脉冲加工熔融石英[117]；(i)裸石英玻璃和带有抗反射结构的石英玻璃效果对比[118]；(j)截锥阵列[119]

Fig. 11　Application of laser fabricated 3D inorganic micro and nanostructures. (a) Femtosecond laser erasure/recovery[66]; (b) QR code encryption demonstration[67]; (c) patterning of $Cl^-Br^-—I^-$ codoped glass[65]; (d) side view of laser welding[112]; (e) assembly drawing of successful laser welding[44]; (f) vertical waveguide in the sensor[7]; (g) microstructure of storage bin[115]; (h) fabrication of fused quartz by circularly polarized laser pulses[117]; (i) effect comparison between bare quartz glass and quartz glass with anti-reflective structure[118]; (j) truncated cone array[119]

3.4　航空航天

航空航天领域的零部件需要耐高温、优良机械性能、高精度等性质来应对极端的外界环境。陶瓷因其低导热系数、低密度等优良性质，成为航空航天零部

件的重要材料。激光加工可以实现陶瓷等材料的焊接及其他加工技术，在航空航天器的组装、修复与维护中发挥着重要作用。Tamaki 等[111]利用飞秒激光在不使用胶水等中间层的情况下实现透明玻璃材料间缝隙小于 $\lambda/4$ 的焊接。Richter 等[112]则实现 3 μm 的均匀间隙焊接，且成功焊接的熔融石英稳定性达原始材料 85%[图 11(d)]，Penilla 等[44]实现了更复杂几何形状陶瓷的高强度连接[图 11(e)]。2023 年 Zuo 等[113]通过对氧化铝激光焊缝裂纹特征进行研究，优化工艺参数，保证了焊接区域母材和焊缝不会产生宏观裂缝，为高质量激光焊接奠定了基础。此外，Royon 等[7]利用激光直写制备了基于溶胶-凝胶光波导传输的传感器，TiO_2-SiO_2 和 ZrO_2-SiO_2 分别作为波导芯层和包层，集成在飞机机翼上。该传感器经过多个波导或处于−40 ℃～80 ℃环境，性能仍不受影响，尤其适用于极端环境下的检测，在航空损伤和分层检测上具有应用前景[图 11(f)]。

3.5　仿生学

激光加工技术能够制备出多种仿生无机微结构，造福人类。Lee 等[114]根据梯度硅基膜模拟原始人类毛细胞频率的选择功能，结合激光剥离制备出柔性无机压电纳米声传感器。Liang 等[115]利用飞秒激光在石英玻璃上刻写新型 3D 仿生光滑表面，该结构将润滑剂储存在内部，在毛细管力的作用下运输到表面，具有良好的表面耐久性和光学透光率[图 11(g)]。2017 年 Liu 等[116]基于飞秒激光结合相位掩模在 ZnS 薄膜上获得大面积的周期性结构。Papadopoulos 等[117]模拟自然界生物表面微结构，首次利用圆偏振超短脉冲激光直接在熔融石英玻璃上产生具有全向抗反射性的纳米柱结构[图 11(h)]。随后，Duan 等模仿自然界蝉和蜻蜓的翅膀，利用飞秒激光微加工技术，在光学玻璃和 MgF_2 表面上分别制备了用于减反射的仿生纳米结构阵列，表现出优良的图像捕捉性能和抗干扰性能[118-119][图 11(i)、(j)]。

4　结束语

激光加工技术无论是在精度还是图案设计自由度上，都呈现出优异的加工能力，广泛应用于科学研究、国防民生等领域[120-121]。近年来，激光加工 3D 无机微纳结构分辨率达到纳米量级，突破光学衍射极限，实现了复杂微纳结构的 3D 制备，为微纳尺度下多种材料高精度的加工提供了基础，也为微纳电子器件、光学微器件、超表面、量子芯片等领域的发展提供了重要支撑。目前，飞秒激光加工 3D 无机微纳结构多采用逐点扫描的方式，加工效率较低，不适合批量化生产。飞秒激光与数字微镜（DMD）结合能很好地解决该问题，通过 DMD 面投影，能够快速地加工出大面积、复杂微结构，大大提高了加工效率[122-124]。Saha 等[125]基于投影逐层打印出宽度小于 175 nm 的纳米线，完成亚微米分辨率的任意复杂 3D 结构。Liu 等[126]提出使用高效跨尺度图案化的无掩模光学投影纳米光刻技术，单次曝光实现最小特征尺寸 32 nm，突破了光学衍射极限，进一步实现了尺寸超数百微米、精度达数十纳米的微结构的快速制备。Wang 等[127]利用无掩模光学投影技术制备 Ag/聚苯胺壳-核结构的纳米复合材料，在多种基底上制备出微纳尺度下的纳米复合图案，且具有一定的导电性和表面增强拉曼特性，为传感器和探测器等微纳器件的制备开辟了新的途径。然而，目前基于 DMD 的飞秒激光加工技术主要针对有机材料，将其与无机微纳结构的加工相结合，必将大大提高 3D 无机微纳结构的加工效率。随着新材料和新技术的不断发展，激光加工制备 3D 无机微纳结构必将在光学、信息、能源、生物工程等领域展示出更为广阔的应用前景。

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