

激光融合制造及在柔性微纳传感器的应用(特邀)

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摘要 柔性微纳传感器的新兴发展对先进制造技术提出了更高要求。其中,激光融合制造充分集成激光增材、等材、减材加工形式,凭借高精度、非接触、机理丰富、灵活可控、高效环保、多材料兼容等特点突破了传统制造在多任务、多线程、多功能复合加工中的局限,通过激光与物质相互作用实现跨尺度“控形”与“控性”,为各类柔性微纳传感器的结构-材料-功能一体化制造开辟了新途径。本文首先分析激光增材、等材与减材制造的技术特点与典型目标材料,展示激光融合制造的技术优势,接着针对近年来激光融合制造在柔性物理、化学、电生理与多模态微纳传感器中的典型应用展开讨论,最后对该技术面临的挑战以及未来发展趋势进行了总结与展望,通过多学科交叉互融,开辟柔性微纳传感器制造新路径,拓展激光制造技术的应用场景。

关键词 激光融合制造; 激光-物质相互作用; 微纳制造; 柔性电子; 柔性微纳传感器

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1 引言

随着可穿戴设备、健康医疗、人机交互等领域的蓬勃兴起,柔性电子技术已成为驱动发展的关键技术之一。其中,柔性微纳传感器作为柔性电子技术的重要体现形式,颠覆了常规刚性器件的物理形态,极大促进了人-机-环境三元互联,是助力智能电子发展的重要力量。在智能皮肤中嵌入柔性微纳传感器,可以灵敏地感知外部压力和形变,常用于机器人、假肢等;在体内植入柔性微纳传感器,可以实现对体内微环境以及药物释放、细胞活动等的实时监测;将柔性微纳传感器应用于手部动作追踪、触觉反馈等方面,可以提升虚拟现实交互的真实感。当前,柔性微纳传感器是欧美日韩等发达国家竞相发展的技术。相比较而言,我国传感器产业发展较慢,高端产品主要依赖进口。因此,中国工程院发布的《全球工程前沿 2020》将“柔性电子制造技术”和“可穿戴多功能集成传感器开发”列为 TOP10 工程研究前沿。中华人民共和国工业和信息化部印发的《基础电子元器件产业发展行动计划(2021—2023 年)》聚焦产品高端提升,其中包括智能传感器、穿戴式设备、电子元器件柔性化和轻型化应用等。由此可见,柔性微纳传感器的新兴发展将赋能新一轮科技产业变革,同时驱动微纳制造技术日益精进。

目前,多种成熟的微纳制造工艺已被广泛应用于各类微纳器件的制造。物理/化学气相沉积法可以制备高性能器件,但通常需要特定环境和昂贵设备,在工业大规模生产方面存在一定挑战;纳米压印技术虽然能实现高分辨制造,但存在流程复杂与成本高昂等问题;印刷法在大面积制造方面具有工艺简单、成本低廉等优势,但通常需要掩模版,而且制造精度受限。另外,多功能柔性微纳传感器的构建通常涉及多种微纳制造工艺的复合联用,以便实现敏感材料沉积、图案化以及微纳结构制造等。当下,柔性微纳传感器正向小型化、集成化、智能化和定制化方向发展,这将对敏感材料的高效多功能制备和微纳结构的灵活可控制造提出更高技术要求。

本文提出“激光融合制造”这一概念,即基于激光增材、等材、减材加工及其复合加工模式来满足多功能柔性微纳传感器器件在多尺度、多维度、多材料异构方面的制造需求。激光融合制造利用激光在时间、空间与能量等方面的多维特性与物质相互作用,并通过调控脉宽、波长、功率、频率和速度等工艺参数诱导材料发生熔融烧结、等体改性、热解烧蚀与刻写去除等物化现象^[1-2],使其在激光辐照与扫描空间内形成具有宏、微、纳观多尺度的特定功能结构与物质,实现跨尺度“控形”与“控性”。激光融合制造凭借作用机理丰富、调控方式

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灵活、高精密加工、多材料兼容等特点突破了传统制造技术在多任务、多线程、多功能复合加工中的局限。此外,激光融合制造兼具非接触、成本低、效率高、可控性强、绿色环保与个性化定制等优势,为各类柔性微纳传感器的结构-材料-功能一体化制造提供了全新机遇^[3-8]。

激光融合制造主要包括增材、等材与减材三种形式。激光增材制造,即利用激光作为局部能量源,将纳米前驱体材料加热熔融(还原),之后经烧结、累加、逐层堆积形成功能结构。铜、银、镍等金属或金属氧化物纳米油墨的烧结(还原)便属于激光增材制造。激光等材制造,即通过激光诱导界面反应,使材料在基本保持初始体量的同时改变其本征组织结构和物化特性。激光减材制造,即主要对材料进行热解、烧蚀、图案化刻写与微纳结构制造,可用于增强压力传感器性能、实现高分辨互联电路制造等。通过上述三种激光加工形式的复合联用,能够同时实现纳米材料的堆叠沉积、敏感介质的物化改性、图案化与微纳结构的精细直写,使柔性微纳传感器的多功能集成与一体化制造成为可能^[9-18],因而有望成为传统微纳复合制造工艺的替代方案。

通过激光融合制造工艺,目前国内外已实现多类柔性微纳传感器,主要包括柔性物理类传感(压力^[19-20]/应变^[21-23]、温度^[24-25]、湿度^[26-27]、流量^[28]、姿态^[29-31]、振动^[32]、角度^[33]等)、柔性化学类传感(唾液^[34]、汗液^[35-37]、呼吸^[38-39]等)、柔性电生理传感(心电^[40-43]、肌电^[42-45]、脑电^[42-43]等)以及多功能柔性传感集成系统^[33,35,46-47]。在柔性物理传感方面,采用激光减材结合

等材诱导改性可以低成本制备湿度传感器^[48],通过综合利用激光作用下的高密度能量与强光热吸收,分别实现传感层图案化与敏感材料物态转变,赋予器件理想的湿敏特性。在柔性化学传感方面,利用多激光融合工艺可以实现气体传感器的一体化集成制备^[49],过程包括电极制造(激光刻蚀)、纳米材料合成(激光沉积)和后镀(激光原位退火)。在柔性电生理传感方面,根据不同类型激光器的加工热效应差异,可以实现大面积可拉伸穿戴式肌电传感器阵列^[50],其过程包含光-化学、光热等多种电子-光子反应机制,最终实现器件图案化刻写、堆叠层烧蚀和弹性体钻孔等。在柔性多模态集成传感方面,激光融合制造综合利用可见光的热效应与短脉冲紫外激光的冷加工依次实现材料沉积、图案化、过孔等功能,赋予器件“绘制”、“擦除”、多层互联等特性,促进了多功能皮肤电子系统的开发^[51]。此外,基于激光增材、等材、减材加工的激光融合制造还可以用于实现柔性电路^[52]/电极^[53-54]、柔性加热器^[55]、柔性光电探测器^[56-58]、柔性储能设备^[59-61]等多类柔性电子器件的一步式加工与系统集成。

目前已有多篇关于激光制造柔性微纳传感器的综述性文章^[5,7-8,62],它们主要就激光合成微纳材料与激光加工微纳结构两方面进行阐述。本文聚焦激光融合制造,从全局视角讨论该工艺在柔性微纳传感器制造中的应用形式,依次介绍了激光增材、等材、减材三种制造方法,并重点分析其加工机理与典型目标材料,突出了激光融合制造在柔性微纳传感领域的技术优势与应用价值(图1)。之后具体展示了激光融合制造在柔性

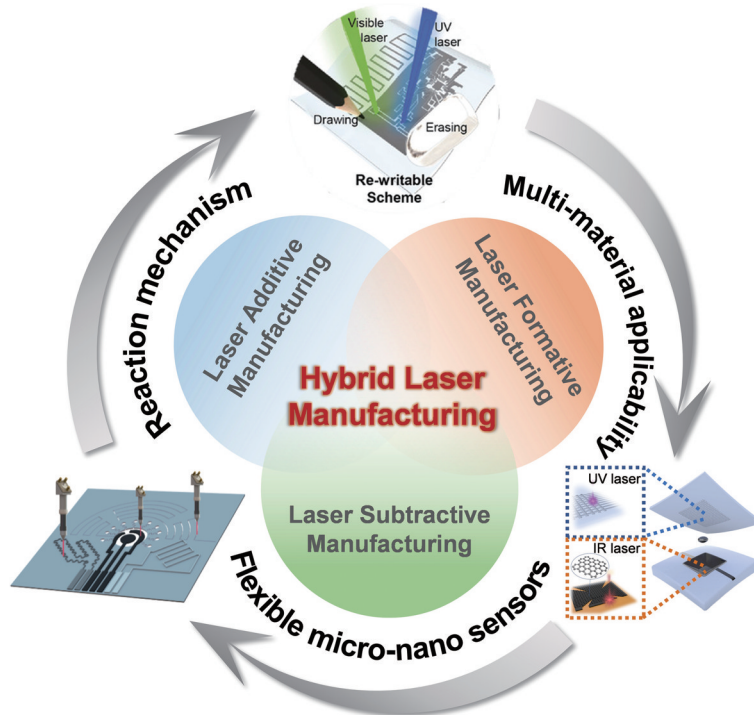


图1 基于激光增材、等材与减材加工的激光融合制造及其在柔性微纳传感器中的应用^[32,35,51]

Fig. 1 Laser hybrid fabrication based on laser additive, formative, and subtractive manufacturing and its applications in flexible micro-nano sensors^[32,35,51]

物理、化学、电生理与多模态微纳传感器中的典型应用,并对相关研究及最新进展进行讨论。最后,针对该领域现存技术挑战进行总结,并对其未来发展趋势进行展望。

2 激光增材制造

2.1 激光增材制造技术特点

利用激光作为高能量源,通过熔化和层压目标材料实现三维结构的逐层构筑,即为“激光增材制造”。迄今为止,基于激光加工的增材制造技术已与各类纳米材料实现良好兼容^[63],如纳米颗粒(NP)^[64-66]、纳米线(NW)^[67-69]、纳米管(NT)^[70-71]、纳米球^[72]等。其中,激光烧结纳米前驱体作为一种快速制备连续导电结构的新路径,可直接在柔性可拉伸基材上形成功能层^[73],目前已被广泛应用于电气互连^[74-76]、感知元件^[77-79]与加热器^[80-81]等。本部分主要讨论激光烧结金属纳米油墨的机理(图2)。

此处以金属纳米颗粒为例,简要介绍激光选择性烧结金属纳米前驱体油墨的过程。如图2(a)所示,当激光的高强度能量冲击到纳米颗粒薄膜表面时,由于光热效应,大部分能量首先被顶层附近的纳米粒子吸收,使其温度迅速升高至熔点。此时,激光辐照区域温度上升,热量持续从薄膜表面传递至其余未被烧结的纳米颗粒,同时引起薄膜内部汽化,这使得油墨中的溶剂蒸发以及有机添加剂、表面活性剂等分解,进而导致膨胀效应。之后,熔融金属纳米颗粒在激光高能聚焦引发的表面等离子体共振效应下形成“颈状”连接,并随比表面积减小而相互融合团聚,长成更大晶粒[图2(b)],最终在激光束选择性扫描的光热作用下重复熔化、凝固,生成均匀连续的导电通路,残余油墨经清洗去除后便完成了图案化加工全过程。值得注意的是,由于目标材料不同,该过程往往还会同时发生光-热-化学诱导还原反应与缺陷结构修饰。例如,对于金属氧化物纳米油墨,激光热能率先使有机还原剂及助剂脱水降解,随后分解产物顺应化学反应机理将高价金属离子还原为金属单质^[82]。

激光烧结技术所产生的高强能量具有局域性特点,而且热效应持续短,可以降低局部热能累积和周围区域温升,不会对底层基材造成长时间、大面积损伤,特别适用于柔性聚合物基材。此外,激光烧结制备的金属导电基质与基材之间通常具有良好界面结合力,这源于基材表面被激光渗透热量部分熔化后冷却凝固,继而与金属薄膜形成互锁嵌合。目前,各种不同波长和脉宽的激光源已经实现了材料烧结^[83]。

综上所述,激光烧结金属纳米油墨作为一种高效获得导电功能层的增材制造方法,可有效克服传统制造工艺存在的材料成本高昂、沉积工序繁琐、导电基质机械特性不足、基底兼容性差等问题。同时,随着激光制造系统的不断升级,纳米功能结构的最小特征尺寸

日益精进,进一步拓展了该工艺的应用范围。

2.2 激光增材制造典型目标材料

金属纳米油墨是激光烧结制造导电功能结构的关键一环,常用的金属纳米油墨主要包括以下几类:1) 单元素金属纳米油墨,如 Au^[84-85]、Zn^[86]、Ag^[87-89]、Cu^[90-92] 纳米油墨等;2) 金属氧化物纳米油墨,如 CuO^[93-94]、NiO^[95]、Cu₂O^[96]、ZnO^[97-98] 纳米油墨等;3) 核壳双金属纳米油墨,如 Cu-Ag 纳米油墨^[99]等;4) 合金金属纳米油墨,如 Cu-Ni 合金纳米油墨^[87]、Au-Ag 合金纳米油墨^[100]、液态金属(LM)合金纳米油墨^[74]等。本部分主要介绍常见的适用于激光烧结技术的几种典型金属纳米前驱体油墨。

2.2.1 激光烧结 CuO 纳米油墨

在非贵金属中,Cu 因具有可媲美贵金属的高导电性与优异成本效益而备受关注^[101]。基于 Cu 纳米前驱体,可利用激光烧结技术完成熔融连接与图案化制造。然而,纳米级 Cu 的氧化势能(约为 0.34 V)较低,很容易在常温环境下氧化,导致烧结时所需能量升高,从而降低了本征电导率。为解决这一问题,研究人员采用空气环境下稳定、成本低廉的 CuO 纳米前驱体,结合有机还原剂、分散助剂等制成纳米油墨,通过激光光热作用诱导化学还原-团聚烧结来高效制备 Cu 导体。

Kang 等^[54]报道了一种通过激光还原烧结工艺生成 Cu 电极的简易制造方法[图2(c)],将 CuO NP 分散在由聚乙烯吡咯烷酮(PVP)和乙二醇(EG)组成的混合油墨中,激光作用时,EG 脱水产生醛基,在不分解 CuO NP 的情况下将其还原为 Cu NP,同时,PVP 分解形成亚甲基、甲胺和甲酸,进一步促进 Cu²⁺ 还原。最后,持续入射的激光能量与转化形成的 Cu 粒子发生光热耦合,继而引发团聚烧结。为深入研究 CuO 在激光增材烧结中的还原趋势, Lee 等^[102]将 PVP 作为还原剂溶于不同溶剂(如异丙醇、乙醇和正丁醇)中,通过调节和优化 CuO 油墨的组分配比,获得了电阻率为 13 μΩ·cm 的 Cu 电极。此外,基于激光选择性重复还原烧结,可以实现 CuO_x 与 Cu 纳米结构间的可逆转化利用。Han 等^[101]借助该工艺在 CuO_x NW 上成功制备出 Cu NW 加热器,证实了其可以直接应用于 Cu 基电子产品的制造。同时,他们基于激光的重复氧化-还原过程,提出“纳米回收”的概念。

2.2.2 激光烧结 NiO 纳米油墨

尽管 Cu 作为 Au、Ag 等贵金属的替代品极具吸引力,但在高温高湿环境与腐蚀性介质中容易氧化失效。相比较下, Ni 具有较高的耐蚀性与耐温性,且色泽与 Ag 类似,适合用作电子器件导体、电化学器件集流器/催化剂、复合材料以及电镀金属等^[73]。然而,目前关于激光烧结沉积 Ni 电极及其应用的报道尚且不多,人们通常选择 NiO 纳米材料用于激光增材制造,在光热作用下同时完成还原和烧结。

Lee 等^[82]基于 NiO_x NP 油墨,利用激光快速图案化分别在玻璃和 PI 基底上制备出高分辨 Ni 电极。其中,油墨含有尺寸极小且分散均匀的 NiO_x NP,致使生成的导电基质层表面形貌光滑。此外,不同于常规油墨体系(以 EG/PVP 作为还原剂),NiO_x 纳米薄膜首先受激光辐照升温,引发薄膜中残留甲苯溶剂分解和 NP 中电子带间激发;随后甲苯分解产生的质子与 NP 提供的自由电子共同参与还原过程;最终,NiO_x NP 被还原至 Ni NP 后熔接成体,完成烧结。与之类似,Nam 等^[55]先通过化学沉淀法和预煅烧 Ni(OH)₂ 大规模合成 NiO_x NP,并配制获得油墨,随后采用激光(还原)烧结在 PET 基底上制备出 Ni 电极[图 2(d)]。与 Cu 电极相比,该 Ni 电极具有优异的抗氧化性。除了单一功能电极制造,由激光烧结产生的独特热激活机制也可以用于提高材料的温敏系数。Shin 等^[24]发现利用激光辐照 NiO NP 油墨层不仅可以促进其光热还原和图案化

烧结,还可以诱导位于两 Ni 电极之间的 NiO NP 快速退火固结,形成 NiO 传感通道,最终集成单片无缝式 Ni-NiO-Ni 异质结构的温度传感系统。该温度传感系统在 25~70 °C 范围内表现出典型负温度系数热敏电阻(NTC)特性,在人造皮肤和表皮温度传感器方面具有一定应用潜力。

2.2.3 激光烧结 Ag 纳米油墨

Ag 作为一种优良的电热导体,已被广泛应用于电子领域。尽管 Ag 的成本高昂,但其作为早期激光数字图案化的核心材料,凭借较好的氧化稳定性和优异的基材附着性,使用频率依然很高^[63],而且由单元素 Ag NP 组成的油墨前驱体仍然是光热烧结制备高性能柔性金属透明导电薄膜、柔性应变传感器、贴片天线、射频识别(RFID)标签等的优先选择。

目前已有较多关于激光直写 Ag 纳米油墨制备电极图案与导电路径的研究报道。例如,Hong 等^[89]通

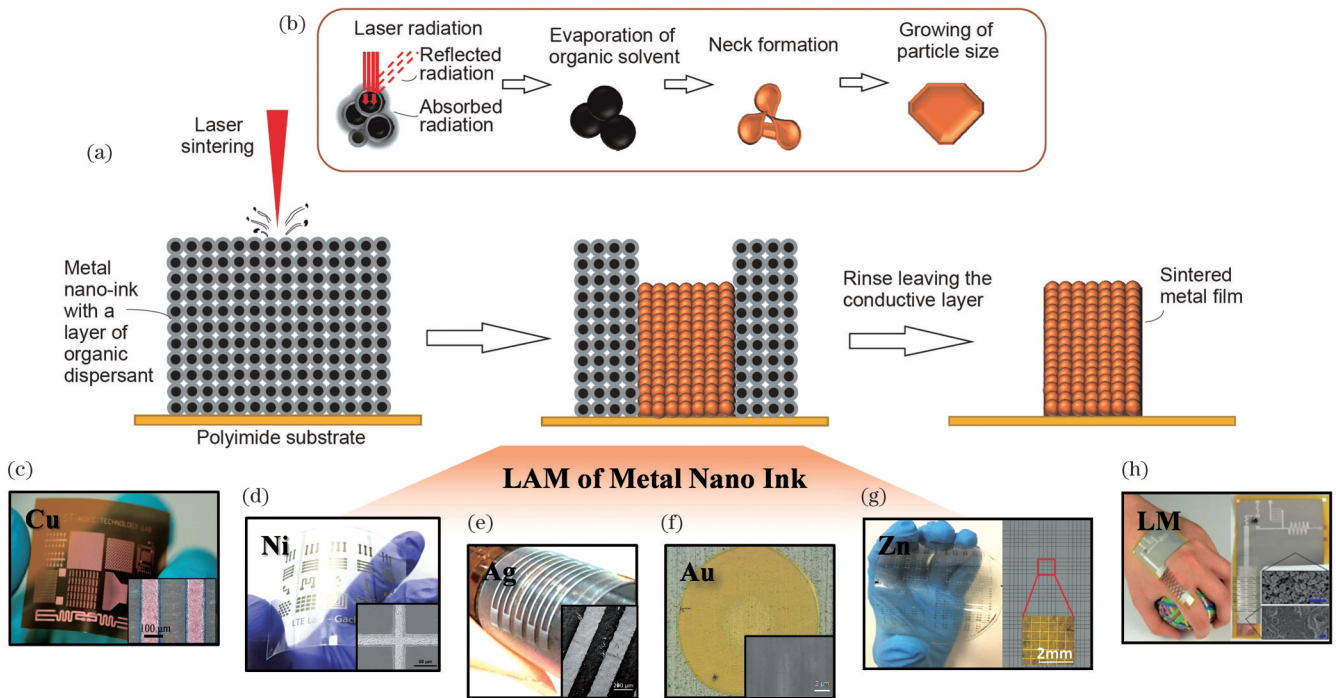


图 2 激光增材制造技术特点及典型目标材料。(a)激光烧结工艺流程简图^[83];(b)激光烧结过程中金属纳米油墨变化过程示意图^[83];(c)PI 薄膜上的 Cu 电极(插图:显微图)^[54];(d)PET 基底上的 Ni 导电图案(插图:放大扫描电镜图)^[55];(e)弯曲并共形附着的 Ag NP 基应变传感器(插图:导电迹线的光学图像)^[23];(f)激光烧结 Au NP 薄膜的光学显微图(插图:放大扫描电镜图)^[84];(g)激光数字印刷烧结的 Zn NP 基瞬态器件阵列和网格图案(插图:Zn 迹线的光学图像)^[85];(h)由沉积在柔性印刷电路板上的激光烧结 LM NP 薄膜组成的柔性可拉伸电子器件照片,其中激光烧结图案(浅灰色)用于在 Cu 走线和集成电路之间创建导线、电阻和电容器(插图:印刷和激光烧结的 LM NP 薄膜代表性区域的 SEM 图像)^[74]

Fig. 2 Technical characteristics and typical target materials of laser additive manufacturing. (a) Schematic diagram of laser sintering process^[83]; (b) schematic diagram of changes in metal nano ink during laser sintering process^[83]; (c) Cu electrodes on PI film (inset: microscopic image)^[54]; (d) Ni conductive patterns on PET substrate (inset: magnified SEM image)^[55]; (e) flexible and conformally adhered Ag NP-based strain sensor (inset: optical image of conductive traces)^[23]; (f) optical micrograph of laser-sintered Au NP film (inset: magnified SEM image)^[84]; (g) Zn NP-based transient device array and grid pattern by laser digital printing and sintering (inset: optical image of Zn traces)^[85]; (h) photograph of a flexible and stretchable electronic device composed of a laser-sintered LM NP film deposited onto a flexible printed circuit board, where the laser-sintered patterns (light gray) are used to create conductive traces, resistors and capacitors between Cu traces and integrated circuits (inset: SEM images of representative areas of the as-printed and laser-sintered LM NP film)^[74]

通过对 Ag NP 油墨进行选择性激光烧结,在柔性 PET 基材上制备出网格状透明导体,其具有较高透光率 (>85%) 和较低方阻 ($30 \Omega \cdot \text{sq}^{-1}$),可应用至触摸屏面板上,在连续机械应力下稳定工作。此外,快速激光烧结可以代替传统热退火工艺,在常温下对印刷 Ag NP 薄膜进行选择性沉积。Yang 等^[103]通过内外弯曲、拉伸、循环疲劳和黏附性测试重点探索了激光烧结纳米 Ag 膜的机械耐久性,以及其在不同高温、高湿条件下的环境稳定性,并与传统热退火 Ag 膜进行对比。结果表明,激光烧结 Ag 膜具有足够的机械可靠性,但若面向极端环境应用,仍需进一步优化其性能。Agarwala 等^[23]使用气溶胶预喷射打印 Ag NP 油墨,接着采用激光在低温绷带基底上热沉积 Ag 薄膜,以制造面向家居健康监测的可穿戴应变传感器[图 2(e)]。通过调控加工参数,他们系统性探究了激光光热效应对纳米薄膜微观结构的影响。结果显示,该传感器具有良好的可拉伸性,在 700 次重复弯曲测试后依旧保持着高灵敏度和稳定性。

2.2.4 激光烧结 Au 纳米油墨

Au 是贵金属中资源稀缺、价格昂贵的代表性材料,虽然这一特性在一定程度上限制了其在大规模柔性电子领域中的应用,但研究人员仍然在实验和理论上对激光烧结 Au 纳米油墨工艺进行了广泛研究。

不断开发更小、更细、更紧密的组件是电子制造业的趋势。面对这一需求,Chung 等^[86]通过激光烧结固化 Au NP 油墨成功制备出电阻率接近块体金的微细线导体。该工作主要借助 NP 油墨制备和 Au 层对激光的吸收来实现油墨中溶剂的蒸发与 Au NP 的沉积。通过调节激光束光强的空间分布可以有效控制生成 Au 线的表面形貌和电学特性。Ko 等^[104]基于选择性激光烧结喷墨打印的 Au NP 油墨,开发出一种实现高分辨率有机场效应晶体管的制造工艺。在激光与 Au NP 相互作用后的共振耦合效应下,局部激光烧结可以减小热影响区,有助于能量沉积,最终完成热敏聚合物基材上低成本、大面积柔性电子器件的制造。为替代电子元件的传统电镀方法,Yamaguchi 等^[84]基于预配制的 Au NP 浆料,采用激光烧结将 Au 膜沉积在镀镍磷青铜基材上[图 2(f)],并通过烧结膜的表征分析探讨激光加工机理。

2.2.5 激光烧结 Zn 纳米油墨

Zn 具有适中的降解速率和良好生物相容性,被认为是典型的生物可吸收植入材料之一,且不会对环境造成二次污染。然而,近年来关于激光增材烧结 Zn 纳米材料的研究还处于探索阶段,其中大多数研究聚焦于可降解 Zn 的成形制造。

为了减小废弃电子垃圾对生态环境造成的危害,开发生物可降解电子器件成为一种有效解决方案。Shou 等^[85]通过密闭蒸发-冷凝介导的激光烧结制备出 Zn NP 薄膜,实现了一种低成本生物可吸收导体的制

造。该工艺以 Zn NP 悬浮液为目标主体,利用激光进行高速扫描,以直接在接收基板上沉积出高结晶度 Zn 迹[图 2(g)]。此外,任意图案化和网格直写也进一步说明了激光烧结工艺的多功能性。在低成本制造瞬态金属电子方面,Feng 等^[105]采用激光烧结工艺对自然氧化的 Zn 微粒油墨进行处理,依靠能量从高能光子到焊接相邻 Zn 粒子的快速转移,成功制造出与生物可降解基质兼容的高导电性与机械耐久性 Zn 导体 ($10^6 \text{ S} \cdot \text{m}^{-1}$),并在柔性近场通信(NFC)器件中创建了 Zn 互连天线。

2.2.6 激光烧结 LM 纳米油墨

Ga 基液态金属凭借其优异的机械顺应性在制造柔性应变传感器、柔性压力传感器、柔性加热器、柔性致动器和柔性天线等柔性电子器件方面具有广阔的应用前景^[106-107]。然而,LM 在环境中容易迅速形成表面氧化膜,屏蔽了其优良导电性,从而限制了它在电子学中的应用^[108-109]。激光烧结技术可以有效破坏氧化层,使 LM NP 核受热凝聚,并通过图案化直写至薄膜基材中,以快速创建柔性数字电路和可拉伸电子器件。

基于上述思路,Liu 等^[74]利用激光烧结 LM 纳米油墨,制备出具有定制化电性能的电容器和电阻器、混合柔性电路和可拉伸电路[图 2(h)]。Xu 课题组^[26]基于一步激光直写技术制备出一种可穿戴式柔性 $\text{Ga}_2\text{O}_3/\text{LM}$ 湿度传感器。在激光光热作用下, Ga_2O_3 包裹的 LM 颗粒在经历热膨胀、氧化层破裂、熔融凝聚、相分离后被选择性烧结,从绝缘态转变为导电态(电阻率为 $0.19 \Omega \cdot \text{cm}$),而未被激光处理的区域作为湿度感知层,用于监测人体呼吸速率以及不同生理状态下手掌皮肤中的水分含量。为实现应变不敏感线路,Cho 等^[110]利用激光诱导的光热反应实现了 LM 微颗粒和 Ag NW 之间的缠绕烧结,在增强该双相金属复合物与基底黏附性的同时,提高了其抗刻蚀能力。此外,通过调整激光功率可以调控 LM 颗粒与 Ag NW 的缠绕程度,使其具有不同的初始电导率和局部应变系数。

3 激光等材制造

3.1 激光等材制造技术特点

通过激光作用引发物理/化学反应,实现对目标材料的改性、修饰即为“激光等材制造”。其中,基于激光加工的等材制造已被广泛用于诱导改性碳基前驱体(如激光诱导石墨烯 LIG 等),生成物具有良好的力学性能与优异的电化学特性,是柔性功能器件中最具前途的材料之一^[111-112]。此外,激光诱导碳化产物可转印至弹性聚合物(PDMS、Ecoflex、SEBS 等),进一步拓展了该技术在柔性可拉伸电子器件中的应用。因此,激光诱导改性可以面向实现柔性电极/电路的精细化加工和敏感材料感知层的个性化定制,同时能够最大限度减少原材料的使用、降低对环境的影响。本部分

主要就激光诱导碳基前驱体生成石墨烯及其衍生物的过程和机理展开讨论(图 3)。

LIG 技术自 2014 年经 Tour 团队^[113]证实以来,便引起了国内外广泛关注。基于激光处理碳基前驱体材料诱导石墨烯及其衍生物的形成,为原位直写石墨烯基柔性电子器件提供了一种可行方案^[114-119]。LIG 的形成在很大程度上取决于激光光源和脉冲宽度^[111]。根据波长不同,用于制备 LIG 的激光源可以分为紫外、可见光和红外三类[图 3(b)],其主要通过光化学和光热效应诱导聚合物改性。具体而言,如图 3(a)所示,光化学或光化学-光热耦合反应通常发生在短波长激光(如紫外激光)作用下,此时吸收的高光子能量可以直接破坏碳基前驱体中的低键能化学键,形成致密的石墨烯结构。若激光通量增加,短波长激光的分子能级和无辐射跃迁过程还会引起额外温升,通过光热诱导聚合物裂解。当采用较长波长激光(如红外激光)时,光热反应将占据主导,富碳前驱体将吸收的入射光子能量转化为局部热量,使得作用区域热能迅速沉积($1000\text{ }^{\circ}\text{C}\cdot\text{s}^{-1}$)并产生极高温($>2500\text{ }^{\circ}\text{C}$),导致目标材料内部晶格振动加剧,进而引发 C—O、C=O、C—N 键断裂和残余碳重组,触发碳化、石墨化过程,同时释放气态产物(CO、CO₂、C₂H₂等),产生瞬态高压环境,最终形成三维多孔石墨烯网络^[119]。对于可见光,光热效应和光化学反应可能同时存在。早期,研究人员主要使用波长为 $10.6\text{ }\mu\text{m}$ 的 CO₂ 激光系统诱导含碳聚合物,但其远红外特性和较大热影响区会导致 LIG 较厚且线径宽。与传统红外激光相比,使用紫外激光制备的 LIG 分辨率更高、均匀性更好,更有利于器件的小型化集成。除了激光波长外,脉宽也是实现 LIG 可定制化生产的重要影响因素。一般来说,具有长脉冲宽度的激光(连续激光、毫秒激光、微秒激光和纳秒激光)主要通过光热效应在短时间内沉积大量能量来加工 LIG 及其衍生物,其间产生的局部高温会破坏材料键合,高压环境会抑制碳前体分解并将小碳团簇聚集为更大的石墨烯团簇,所释放气体会降低石墨结构转变时的氧化程度。然而,在追求高精度石墨烯图案时,由于热效应可控制度较低,通常会改用具有高瞬时输出功率的超快激光(皮秒激光和飞秒激光),以诱导其与碳基前驱体的非线性相互作用。此外,LIG 的形成还需要达到临界温度($2700\text{ }^{\circ}\text{C}$)以上才能将 sp³ 碳转化为 sp² 碳并形成石墨烯芳香族网络结构。倘若激光能量较低(如低通量脉冲激光),碳化产物则主要以非晶碳(AC,一种 sp² 碳嵌入 sp³ 碳基体的混合物)形式存在。

接下来以 PI 为例,针对其向 LIG 转化过程中的碳前驱体粒子形态演变进行分析。如图 3(c)所示,当激光沿碳化路径扫描基材时,PI 粒子局部升温,引发化学键断裂,随后升华原子重新结合形成气态产物,导致 PI 颗粒膨胀,气体通过颗粒间的孔隙排出,最终生成

三维泡沫状石墨烯结构^[120]。

综上,激光诱导碳基前驱体生成石墨烯及其衍生物作为一种典型的等材制造方法,将 LIG 合成和图案化一步融合,既避免了传统制造技术(如机械剥离、化学气相沉积、外延生长、还原氧化石墨烯)制备条件苛刻、化学处理繁琐、反应设备昂贵、生产效率低和能耗较高等缺点,又为进一步材料掺杂和结构功能化创造了可能^[121-122],是一种灵活、可定制和可扩展的生产方式,已被成功应用于高性能柔性微纳传感器^[123-128]、能源装置^[129-131]、可穿戴设备^[132-134]、智能服装^[135-136]、智能组件^[137-138]和绿色电子产品^[139-149]等多功能电子领域。

3.2 激光等材制造典型目标材料

在早期研究中,只有 PI、PEI 和 PAI 等富含芳香族及酰亚胺重复单元的材料可以被激光诱导转化为 LIG^[115]。近年来,研究人员通过对 LIG 工艺进行大量探索发现,大多数含碳材料,如布料^[135-136]、纸张^[139,150-151]、食物^[114-115]、聚合物^[152-154]、木材^[138]、树叶^[149]等,在合适的激光加工参数下均可实现 LIG 制造。同时,碳源多样化也为回收废物再利用、开发功能电子器件开辟了一条新路径。本部分主要就几类典型碳基前驱物基底在激光等材诱导 LIG 中的应用展开介绍。

3.2.1 含碳布料前驱体

可拉伸、可穿戴式柔性电子器件备受欢迎,而具有编织结构的碳材料正逐渐成为一种研制新选择^[155]。目前,开展激光诱导含碳布料前驱体的研究已成为国内外热点。

将多功能电子器件集成到服装布料中可以定制纺织电子产品,基于这一思路,Wang 等^[136]通过直接在 Kevlar 高分子织物上写入 LIG,制备出一种正面为多孔石墨烯、背面为纤维结构的一体化自供电智能防护服,其兼具穿着舒适和检测有毒 NO₂ 气体的功能。在透气、灵活、高灵敏氮氧化物气体传感器制备方面,研究人员也进行了探索。例如,Yang 等^[135]基于激光等材工艺,将自组装嵌段共聚物(BCP)/树脂复合体经光热转化为高孔三维 LIG 泡沫,同时嵌入 Ag NP 进行修饰,在 Kevlar 等多种织物基底上获得了高性能柔性气体传感器(检测限低至 10^{-9} 量级)[图 3(d)],展现出智能服装的发展潜力。考虑到以蚕丝为前驱体制备 LIG 基柔性器件具有可行性,Li 等^[156]以低成本、环境友好型真丝织物为原料进行预热处理和激光碳化,获得了 $40\text{ }\Omega\cdot\text{sq}^{-1}$ 的 LIG 薄片电阻,并成功实现用于可穿戴设备的柔性应变传感器。其中,织物纤维结构外壳为多层缺陷石墨烯,内层为中空态,两者协同赋予产品以良好的透水、透气性,已被用于湿度和气体感知。

在激光诱导富碳布料前驱体生成 LIG 方面,Tour 团队发现可以利用多重激光处理将其先转化为无定形碳,随后再基于激光束重复照射逐渐实现石墨化。Chyan 等^[114]通过上述方法在经过预阻燃处理的纱布、

平纹棉布、帆布、牛仔布和粗麻布上成功获得了 LIG [图 3(d)]。

3.2.2 含碳纸张前驱体

纸张作为一种环保低成本基材,适用于可丢弃、可回收和环境友好型柔性电子产品(如摩擦发电机、纸基电池、超级电容器、传感器、执行器、微流控系统^[139-140])的制造。然而,传统的纸基电子系统主要通过蜡印、蒸发、光刻等方法沉积贵金属,大大增加了制造成本。为了充分利用纸张的可生物降解特性,探索绿色可持续循环的电子产品制造技术,基于激光诱导碳化纸基前驱体的工艺应运而生^[150-151]。

清华大学研发团队^[157]利用激光碳化在 Nomex 纸张表面制造出多孔石墨烯,并基于双面导通 LIG

在单个器件上同时实现了压力传感和高分辨发声。如图 3(e)所示,Zang 等^[140]开发出一种基于多孔碳化铅-石墨烯(MCG)复合电极的纸基电子器件,MCG 复合电极具有良好的机械稳定性,在结合 Origami 折纸设计后可构筑出 3D 立体化电子元件。Jung 等^[139]设计了一种内置传感器的智能包装纸,其由 LIG 和商业食品包装纸复合而成,可用于实时监测食品保鲜度。LIG 的高表面积有助于感知食物变质后的分解气体三甲胺(TMA)和温度状态,监测数据通过无线通信在移动设备上实现可视化获取。作为概念验证,该纸基传感器已被原位制造在牛奶盒和纸杯上,有望为下一代绿色电子产品的低成本、定制化制造提供思路。为了充分挖掘天然纸基材料的潜力(如可回收性、自然溶解性、

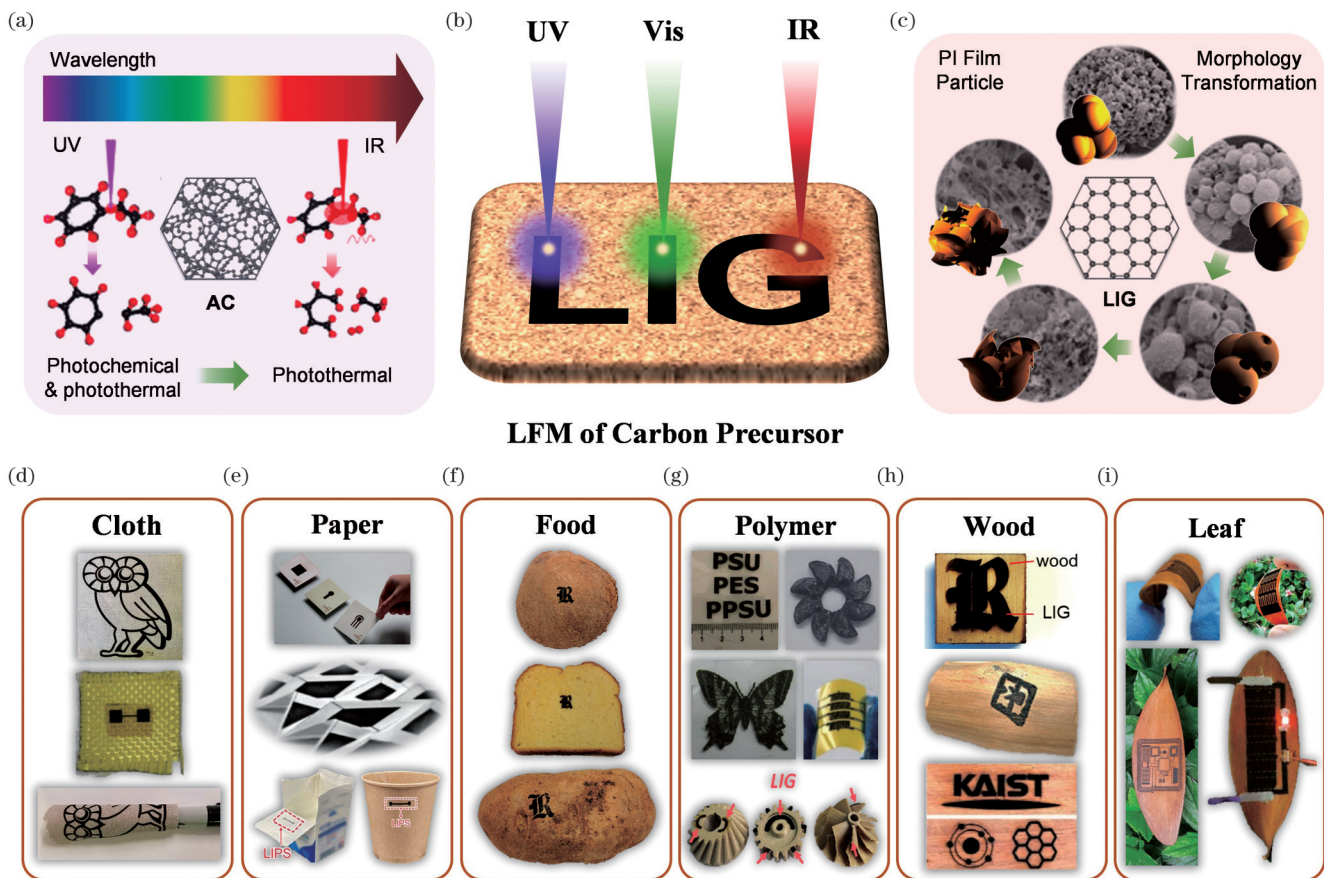


图 3 激光等材制造技术特点及典型目标材料。(a)不同波长激光制备无定形碳与 LIG 的示意图^[119];(b)利用各种激光源和碳前驱体制备 LIG 的示意图;(c)激光碳化 PI 生成 LIG 过程中碳前驱体粒子的形态演变^[120];(d)基于含碳的布料前驱体生成 LIG 及其衍生物^[114,135];(e)基于含碳的纸张前驱体生成 LIG 及其衍生物^[139-141];(f)基于含碳的食物前驱体生成 LIG 及其衍生物^[114];(g)基于含碳的聚合物前驱体生成 LIG 及其衍生物^[137,142-145];(h)基于含碳的木材前驱体生成 LIG 及其衍生物^[146-148];(i)基于含碳的树叶前驱体生成 LIG 及其衍生物^[11,149]

Fig. 3 Technical characteristics and typical target materials of laser formative manufacturing. (a) Schematic of fabrication of amorphous carbon (AC) and LIG with different wavelengths of laser^[119]; (b) schematic of fabrication of LIG using various laser sources and carbon precursors; (c) morphological evolution of carbon precursor particles during laser carbonization of PI to LIG^[120]; (d) generation of LIG and its derivatives from carbon-based cloth precursors^[114,135]; (e) generation of LIG and its derivatives from carbon-based paper precursors^[139-141]; (f) generation of LIG and its derivatives from carbon-based food precursors^[114]; (g) generation of LIG and its derivatives from carbon-based polymer precursors^[137,142-145]; (h) generation of LIG and its derivatives from carbon-based wood precursors^[146-148]; (i) generation of LIG and its derivatives from carbon-based leaf precursors^[11,149]

无有害残留物), Cantarella 团队^[141]将加工水果废料中获得的纸质基材与激光直写技术相结合,在不同纸张(苹果纸、葡萄纸、猕猴桃纸)上进行参数优化,制备出一次性电极,并应用在人体皮肤上实现可靠监测心脏和呼吸活动,同时它还可以作为纸基阻抗光谱器件用于智慧农业。

3.2.3 含碳食物前驱体

随着激光工艺的扩展,LIG 图案可以在多种碳前驱体基材上生成^[116],用于柔性、可生物降解甚至可食用电子产品的开发。目前已经能够在特定食物上制造 LIG[图 3(f)]^[144]。

Tour 团队发现含有木质素的碳前体在惰性气体或还原性受控气氛中可以通过激光处理转化为较高质量的 LIG,这表明交联芳香结构有助于形成石墨烯。椰子壳、马铃薯皮等天然材料的木质素含量较高,即使在大气环境下加工,经脉冲激光多次直写碳化后也能转化为 LIG^[115]。Chyan 等^[144]在椰子壳表面制备出 LIG 微型超级电容器,该电容器具有较高的面电容。此外,基于食物基材的激光诱导碳化还可以扩展至面包^[148]、柚子^[158]等,所产生的功能性 LIG 在温度、湿度、紫外线、气体传感方面均可发挥作用^[148]。

3.2.4 含碳聚合物前驱体

大多数含碳的高性能聚合物材料,包括热塑性、热固性和天然聚合物,在合适的激光条件及工艺参数下均有望转化为 LIG^[159]。PI 作为热塑性聚合物的典型代表,在材料稳定性、耐高温和柔韧性等方面表现优异,也是早期 LIG 研究中最常用的碳源^[115]。具体而言,商业 PI 膜经 CO₂ 激光处理后颜色由橙色变为黑色,对应拉曼光谱显示出以 2700 cm⁻¹ 为中心的突出二维峰,这表明生成了石墨烯结构^[113]。

近年来,随着 LIG 制备技术的快速发展,其他常见聚合物,如 PEEK^[152]、PPS^[153]、PSU^[142]、PES^[160]、PPSU^[161]、PDMS^[154]、PR^[162]、PTFE^[129] 和光刻胶^[163] 等,均已被证明可以制备 LIG,部分如图 3(g) 所示。Hu 等^[164] 基于碳纤维增强聚醚醚酮(CFR-PEEK)所具有的低密度、X 射线透明度、良好生物相容性以及类人体骨骼模量等特性,通过激光碳化直接在其表面原位制造出应变传感器,并用于实时评估骨折愈合和假体失效情况,有望代替传统刚性金属骨科植入物,助力个性化医疗诊断。类似地,PEEK-LIG 智能构件在深海、太空等极端环境中也具有一定应用潜力。Yang 等^[137] 利用激光在 PEEK 基齿轮上原位加工出 LIG,分层石墨烯作为敏感层能够自主监控多环境下的工作状态和变形情况(如旋转和磨损)。在耐热聚合物中,PR 常用于合成碳复合材料和活性炭前驱体,然而,以往的 PR 基衍生碳材料制备通常需要在惰性气氛下进行长时间高温加热,而且纯 PR 对光的吸收较弱。为了探究 PR 是否能与 LIG 技术兼容,Zhang 等^[144] 将激光石墨化 PR 与多种有机染料或金属盐等光吸收剂进

行掺杂,成功实现了高导电性的三维多孔石墨烯图案,并应用于超级电容器和电化学传感器中。此外,激光诱导碳化还能生成聚合物基特定功能层。Wang 等^[143] 利用激光处理 PDMS 表面,形成具有独特疏水性的高效光热层,该表面可以在光驱动超疏水浮动装置中发挥作用。

3.2.5 含碳木材前驱体

木材作为一种丰富的可再生、可回收自然资源,开发与之相关的生物降解、环保型木制电子产品将有助于减少日益增长的电子垃圾问题^[165]。从木材中获得高导电性 LIG 可以激发未来多功能绿色电子器件的可持续发展[图 3(h)]。

研究表明,木质素含量高的木材所固有的交联纤维素结构比木质素含量低的木材更有利于生成高质量石墨烯。莱斯大学的 Ye 等^[146] 利用 CO₂ 激光在特定环境(室温常压、氩气或氢气保护气氛)下辐照松木,将其表面转化为良好的石墨烯导体(方阻 $\approx 10 \Omega \cdot \text{sq}^{-1}$)。他们发现此过程中隔绝氧气至关重要,这使得木材在被诱导改性的同时不发生燃烧,仅生成石墨烯泡沫皱状薄片,与木材表面紧密黏结。此外,通过改变激光强度还可以改变 LIG 的化学组成和热稳定性。

随着激光光源多样化和 LIG 技术精细化, Kim 团队^[11] 在空气环境中采用超快高光子能量激光脉冲在天然木材上实现了高导电性石墨烯图案的一步式直写,并用于制备高能量密度超级电容器。该方法首先通过高重复频率的紫外飞秒激光脉冲将木材转变为中间焦炭,再通过直接光转化过程将其连续转化为 LIG。由于热预算较低且烧蚀程度小,LIG 在未经任何预处理的情况下能够直接在木材表面形成高分辨图案。

在集成应用方面,基于木材的 LIG 同样可以在智能家居中发挥作用。Nam 等^[138] 展示了利用飞秒激光直写技术制造木源 LIG 电子单元。通过形成 LIG 基温度传感器、加热器等,可构建基于物联网的绿色木制家居智能组件。此外,该技术还可以用于机械组装木块上的互连线路/电极,其可作为低成本和可生物降解的绿色电线替代品。

3.2.6 含碳树叶前驱体

尽管木材基 LIG 在生产成本和生态友好性方面具有明显优势,但其制备条件普遍较为严苛,而且无法实现共形贴附。因此,寻找一种用于 LIG 合成的通用绿色前驱体成为了探索趋势。其中,树叶作为天然肥料的重要来源,具有资源丰富、绿色可再生、生物可降解等特点,它们大部分由生物矿物质组成,可作为生产三维纳米石墨烯的前驱体模板[图 3(i)]。同时,树叶薄而柔韧,有望成为柔性可穿戴电子产品的基体材料^[11]。

Le 等^[149] 利用聚焦紫外飞秒激光束直接在空气环境中基于自然落叶制造出任意石墨烯图案。研究发现,叶片对紫外光具有高吸收率,因此紫外光是一种

可将叶片中的天然生物矿物质转化为无机晶体的理想光源。该无机晶体可以作为介孔少层石墨烯生长的成核位点。在石墨化诱导过程中,利用重复激光脉冲的热量累积可以精确控制叶片基底温度,实现叶片有效碳化;利用超强激光脉冲的极高瞬时温度可以将非晶碳进一步转化为石墨碳。此外,超短激光脉冲还可以在加工辐照位点诱导超快加热速率,以促进石墨烯形成。利用以上技术制得的 LIG-无机混合微电极具有优异导电性(方阻低至 $23.3 \Omega \cdot \text{sq}^{-1}$),可作为高性能柔性微型超级电容器(在 $5 \text{ mV} \cdot \text{s}^{-1}$ 下的面电容为 $34.68 \text{ mF} \cdot \text{cm}^{-2}$,在 50000 次充放电循环后的电容保持率约为 99%),为 LED 或电子台钟供电。

4 激光减材制造

基于激光精确可控的热效应以及直接能量去除机制对材料进行图案化刻写/切割、烧蚀/热解和精细微纳结构制备即为“激光减材制造”。其中:激光刻写/切割可用于获得特定轮廓形状的图案和器件,尤其是小尺寸、微型化器件;激光烧蚀/热解可实现对材料的高效、高质量去除,实现精密微加工;激光微纳结构可跨尺度形成多级复合结构,并动态调控材料的界面性能(例如,激光诱导周期表面结构(LIPSS)技术相较于烧蚀工艺可以生成更为复杂的表面纳米结构)。本部分主要就激光对几种典型材料的热解、烧蚀、切割与 LIPSS 的减材过程及机理展开讨论(图 4)。

物质在聚焦激光高温作用下受热分解的反应即为“激光热解”,该工艺常用于生成生物传感器敏感材料^[166]和微通道制造^[167]。这里以韩国首尔国立大学 Ko 团队实现 PDMS 高效三维成形的工作^[168]为例,对激光热解过程进行介绍。当激光以黑色油墨作为引发剂辐照在 PDMS 上时,其表面热解起始点区域的组分被转化为非透明 SiC 层;随着黑体 SiC 的吸光度增加,激光热能进一步增加,这使得激光聚焦几微米范围内的 PDMS 基材持续热解,并引发热解诱导的连锁反应,最终通过激光正表面扫描技术沿辐射路径完成 PDMS 结构的加工[图 4(a)]。与传统 PDMS 激光刻蚀成形技术相比,激光热解工艺的加工质量显著提升,而且具有较高的图案分辨率。此外,该团队还进一步开发出背面扫描技术,通过逐层形成 SiC 实现了 PDMS 基底内部(几毫米纵深方向)的热解成形。以上技术可以通过调控激光强度、扫描速度等工艺参数快速构造不同的 PDMS 二维图案和三维结构,具有高度可控性。同时,该技术可取代多步骤、耗时长和成本高的软光刻工艺,在短时间内构建高质量 PDMS 基有形器件。此项研究成果在微流体系统、软体机器人[图 4(b)]和生物芯片等微结构器件方面均展示出巨大的应用潜力。

目标材料在高功率激光诱导的瞬时高温下被选择性去除即为“激光烧蚀”,其常用于制备多功能传感

器^[169-170]、功能性超亲水^[171]/疏水^[172-173]表面、表面增强拉曼散射(SERS)基底^[174-176]和导电电极^[177-178]。图 4(c)展示了利用飞秒激光烧蚀生成的结构化表面来制备超疏水/亲水性混合基底^[170],以改善 SERS 的性能。Yu 等^[170]通过在超疏水结构附近形成微孔来避免沉积物分布在中心区域,从而进一步增强靶分子富集,实现对小范围超低浓度分析物的灵敏检测。在可回收高性能 SERS 基底的制备方面,Xu 等^[175]受刺猬状结构启发,先采用纳秒激光烧蚀对铜片进行周期性微槽阵列直写,形成 V 形微米结构,随后通过热氧化在微槽侧壁上生成高密度分层 CuO NWs,二者共同构成双尺度微纳结构。由此制造的 SERS 基底不仅增强了对宽带可见光的吸收能力,甚至将吸光波段扩展到近红外范围。此外,该基底与 CuO NWs 复合材料具有良好的界面结合力,在 7 次循环测试后的 SERS 活性依旧保持在 85% 以上。在激光构筑超疏水功能表面方面,一个典型的例子是 Wang 等^[179]采用超快激光烧蚀结合化学蚀刻等方法制备出 4 种不同微纳结构的超疏水表面(规则微米柱-纳米颗粒二级表面、不规则微米凸起-纳米颗粒二级表面、微米柱单级表面以及化学蚀刻不规则微纳表面)。他们对这 4 种表面开展了系统性结冰/融冰研究,结果显示:在超快激光制备的规则微米柱-纳米颗粒二级超疏水表面上,液滴在结冰与融冰循环后可自发恢复至原始 Cassie 状态,其接触直径恢复率和接触角恢复率分别高达 97.8% 和 98.5%,而且融化后的液滴在 3.7° 倾角下能够快速脱离。相比较下,其他表面均无法自发地从 Wenzel 状态恢复到 Cassie 状态。此外,通过激光烧蚀进行微纳结构加工还可以用于调节液态金属的黏附性。Xu 课题组^[32]利用激光直写技术制备出一种全软体自驱动振动传感器。如图 4(d)所示,他们基于紫外脉冲激光的冷加工效应,分别在传感器腔体内的 PDMS 和碳电极表面“雕刻”出微米级网格阵列结构,该结构可以避免液态金属与相邻表面的黏附,从而确保振子在腔体中的自由运动。

采用线偏振激光脉冲多次照射固体材料表面形成自组织微纳结构即为“LIPSS”。与传统光刻和激光直写等方法相比,LIPSS 可以在大范围内实现具有亚波长特征结构的并行加工^[180],而且结构周期和方向等取决于激光波长、激光脉宽、脉冲能量、脉冲数、偏振方向和物质类型^[181],几乎适用于所有材料^[182-183](如金属、玻璃、聚合物和半导体等),是一种可有效实现表面纳米图案化的激光加工技术,目前已在仿生结构着色^[184]、润湿性调控^[185]、SERS^[186]、太阳能热转换^[187]、防冰^[188]和数据存储^[189-190]等方面得到了广泛应用。如图 4(e)所示,Qu 团队^[191]利用无掩模、一步式飞秒激光光刻技术在绝缘体硅器件上制备出可控平面光子结构。在适当的脉冲注入量下,绝缘硅(SOI)晶圆上呈现出高均匀性的亚波长光栅[图 4(f)],并且通过对激

光脉冲进行圆柱形聚焦可以有效实现光栅的大面积制造。他们测量了所制备结构的光学性质,结果显示其具有强大的衍射和光耦合特性。与基于熔体流动的非均匀结构相比,SOI器件的SiO₂层在控制飞秒脉冲注入过程中的相变方面发挥了关键作用。尽管LIPSS可创建各种高要求功能表面,但其也存在顺序扫描时易产生结构错位的问题,这会导致表面结构不均匀,限制了大面积长程有序制备。为了克服上述不足,Huang等^[180]基于对LIPSS不均匀性电磁起源的理解,提出了半周期错配光学增强效应(h-MOE)源于表面等离子体干扰的机制,并以此诱导LIPSS半周期错配排列,从而制备出大面积长程有序均匀结构,生成的纳米图案可扩展至超直光栅、方向可控光栅和半周期不匹配纳米孔阵列。

利用高能密度激光束直接在目标材料表面产生高强度应力场,使其价键结构迅速瓦解,并随光束移动在材料上形成连续切缝从而实现材料分割,即为“激光切割”。近年来,激光切割技术已被广泛用于制备各类柔

性微纳传感器^[192-195]和储能电子器件^[196-197],该工艺具有制样简单、成本低廉、可加工各种原材料和开发不同功能等优点^[198]。Ko团队^[199]利用紫外脉冲激光在AgNWs/cPI上刻写出Kirigami图案[图4(g)],并将其转变为多种重构形状(单轴、双轴和方形螺旋切割结构)。结果显示,所制备出的导电电极在保持超薄弹性的同时还具有高透明度和良好导电性,可以满足多样化拉伸需求,在柔性透明加热器(用于个体热处理、可穿戴式热感和伤口愈合监测)、电子皮肤(用于检测电生理信号)、人机界面演示等方面具有一定的应用价值。同样是面向可拉伸电子应用,Xu等^[200]提出一种激光处理的石墨烯基应变传感器。该传感器以激光刻写Kirigami结构为骨干,在其周围引入Ecoflex,以保护有源传感层表面,同时增大应变分布[图4(h)]。其兼具高拉伸性(应变>200%)、高灵敏度(应变为60%时电阻变化>80%)和高稳定性(>60000次拉伸循环后性能几乎不下降),可用于运动检测和呼吸监测,为下一代可靠穿戴电子产品的开发提供了思路。

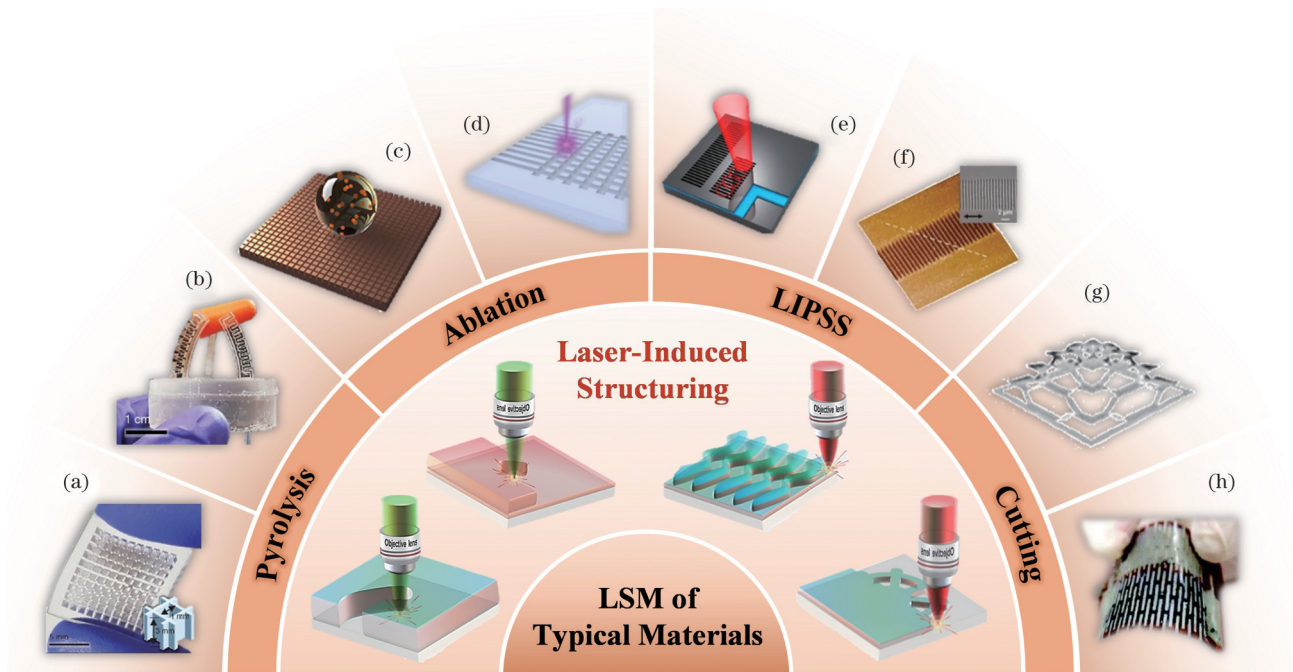


图4 激光减材制造。热解:(a)基于激光背面扫描的高纵横比三维PDMS阵列结构^[168];(b)由PDMS气动手指组成的软机器人手在无重力阻力状态下抓取物体的示意图^[168]。烧蚀:(c)飞秒激光加工复合超疏水/亲水多微孔SERS基底并用于超痕量分子拉曼检测^[170];(d)紫外激光刻写PDMS纹理化表面^[32]。LIPSS:(e)飞秒激光诱导绝缘硅表面生成高度均匀可控的光子结构^[191];(f)绝缘硅器件上高均匀亚波长光栅的三维形貌图(插图:扫描电镜图)^[191]。切割:(g)紫外激光数字切割的可拉伸透明Kirigami电极^[199];(h)激光辅助制造的Kirigami结构可拉伸应变传感器^[200]

Fig. 4 Laser subtractive manufacturing. Pyrolysis: (a) high-aspect-ratio 3D PDMS array structures fabricated by laser back surface scanning^[168]; (b) schematic diagram of a soft-robotic hand consisting of PDMS pneumatic fingers grabbing an object without gravitational resistance^[168]. Ablation: (c) femtosecond laser-processed hybrid superhydrophobic/-philic microporous SERS substrate for ultratrace molecular Raman detection^[170]; (d) UV laser engraving of PDMS textured surface^[32]. LIPSS: (e) femtosecond laser-induced formation of highly uniform and controllable photonic structures on an SOI surface^[191]; (f) 3D topography image of highly uniform subwavelength grating on an SOI device (inset: SEM image)^[191]. Cutting: (g) stretchable transparent Kirigami electrode by UV laser digital cutting^[199]; (h) Kirigami-structured stretchable strain sensor by laser-assisted fabrication^[200]

5 激光融合制造在柔性微纳传感器上的应用

5.1 柔性物理传感器

在电子皮肤、医疗保健和物联网等高端应用中,实时监测各种物理参量(如压力、应变、温度、湿度、振动等)是必不可少的。激光融合制造凭借其在微纳敏感材料和功能结构单元制备方面的一体化优势,已成为开发柔性物理传感器的先进制造技术。

柔性应变传感器作为柔性物理传感器的典型代表,近年来引起了广泛关注,尤其是基于皮肤的可穿戴电子设备^[201-204]。然而,对于目标系统的复杂状态监测(如预测精确的手指运动)往往需要多个应变传感器,在不创建传感器网络的情况下实现对目标对象的全状态测量便成为软电子学的重要研究方向。基于此,Ko团队^[205]介绍了一种集成深度神经网络的皮肤传感器。他们利用激光烧蚀加工出周期性蛇形结构,使传感器富有更大弹性变形,保持与皮肤的共形接触;同时,利用激光退火诱导裂纹层,将其作为传感元件,检测微小机械刺激[图5(a)]。手指运动时,将触发手腕处的皮肤形貌变化,继而应变电信号被传送到皮肤传感器[图5(b)]。最后结合深度学习模型分析信号模式,便可以揭示数据背后的多种手指运动,实现单一皮肤传感器实时解码手部复杂动作。该项技术为健康监测、运动追踪和软机器人技术提供了新路径。

当前,大多数应变传感器的研究主要集中在提高灵敏度和可拉伸性上,为了保证实际设备的可应用性,在不牺牲灵敏度的前提下实现稳定重复的可拉伸和可扩展也是开发应变传感器的关键。基于上述思想,一种激光处理的可拉伸石墨烯基应变传感器被成功制备^[200],其具有高稳定性的核心是减小器件在拉伸条件下的应变。该传感器以Kirigami结构为骨干,在二维至三维面外变形过程中,Kirigami结构内的应变分布增大,赋予了器件优异可逆性。如图5(c)所示,首先利用激光诱导PI-LIG片层与丝网印刷Ag电极形成导电触点,随后通过激光切割形成Kirigami结构。整体装置使用Ecoflex弹性体进行网格包裹和薄膜封装,其中,网格包裹法赋予器件高拉伸性(应变 $>200\%$),薄膜封装法赋予器件高灵敏度(应变为 60% 时电阻变化 $>80\%$)。由于传感器内的应变较小,即使经过 >60000 次拉伸循环测试,其性能也几乎没有下降。考虑到更好的用户体验,Xu等^[200]还在Kirigami结构上印刷了Ag金属互连层,以实现系统的平面集成[图5(d)、(e)]。作为概念验证,该应变传感器在附于人体腹部上时成功检测到由呼吸造成的腹部扩张、收缩过程中实时产生的阻力变化(呼吸周期为 $3\sim 4$ s,持续时长 >2 h)[图5(f)]。检测结果与健康成人的呼吸速率相吻合,这表明该传感器在可

穿戴人机界面中具有一定的应用前景。尽管基于Kirigami结构的柔性应变传感器在长期循环测试中可以保持良好的传感能力,但在制造精度和灵敏度方面仍有待提高。

在实际应用中,压力传感器能够检测到各种身体运动信号和生物信号,如轻微触摸、手腕脉搏、心跳、呼吸频率等,具有重要意义。过去10年内,研究人员已经开发出大量柔性可穿戴压力传感器^[206-208]。为了同时实现高空间分辨率和低串扰干扰,Li等^[206]展示了一种利用两步激光工艺制造的高分辨率柔性压力传感器阵列,其中单个传感像素及其互连分别通过激光低功率诱导碳化和高功率烧蚀形成[图5(g)]。在加工过程中,对激光扫描路径进行编程定义,可以分别在功能层PI和PDMS之间创建蛇形互连结构[图5(h)]。该器件实现了分辨率为 0.7 mm(像素尺寸为 0.4 mm,像素距离为 0.3 mm)的 8×8 传感阵列[图5(i)],单个像素具有 1.37 kPa⁻¹的高灵敏度、 80 kPa的宽压力工作范围、 20 ms的快速响应时间以及良好的周期稳定性[图5(j)],目前已被成功应用于触觉模式识别和微创癌症手术肿瘤组织识别中。

此外,在追求综合性能优越的柔性触觉电子皮肤传感器方面,人们基于电容传感原理,结合双面微金字塔介质层和LM电极,制造出一种高灵敏(2.78 kPa⁻¹)全柔性触觉传感器[图6(a)]^[209],其检测下限低(≈ 3 Pa)、耐久性优异(>10000 次循环载荷)、响应速度快(80 ms)。具体而言,该项工作利用飞秒激光的加工优势实现了以下结果:1) 双面微金字塔介电层的可编程、高效率、低成本、大规模烧蚀制备,所制备传感器相较于先前报道的LM基压力传感器^[210-215]能够显著增强传感信号[图6(c)];2) 通过创建富NP基表面结构赋予微金字塔超疏金属特性,以防止LM浸润并提高电极耐久性[图6(b)];3) 在PDMS基体外表面进行超疏水处理,使器件整体具有优异的表面防污性,并在高湿环境下稳定传输传感信号,从而有效解决水基污染物引起的基电容位移[图6(d)]。由于采用全柔性材料,该触觉传感器在各种复杂变形下也表现出强传感能力,能够监测到人体的生理和运动信号[图6(e)]。

基于全激光直写方法,Xu等^[32]提出了一种全软体自供电振动传感器[图6(f)],该装置由完全可延展的材料构成,包括LM内核和PDMS弹性体外壳。首先利用红外激光在PI基底上加工出图案化LIG,并将平面LIG/PI倒附在模具浮雕上,形成异形曲面碳电极;随后经浇筑PDMS、固化、转移后,获得振子的LIG/PDMS弹性体活动腔室。为了保证LM液滴在腔内自由振动,使用紫外脉冲激光分别在凹形LIG/PDMS和扁平PDMS盖帽上雕刻出网格状微尺度纹理[图6(g)、(h)]。该振动传感器利用LM液滴和PDMS弹性体的摩擦起电效应输出振动信号,其基于自由液

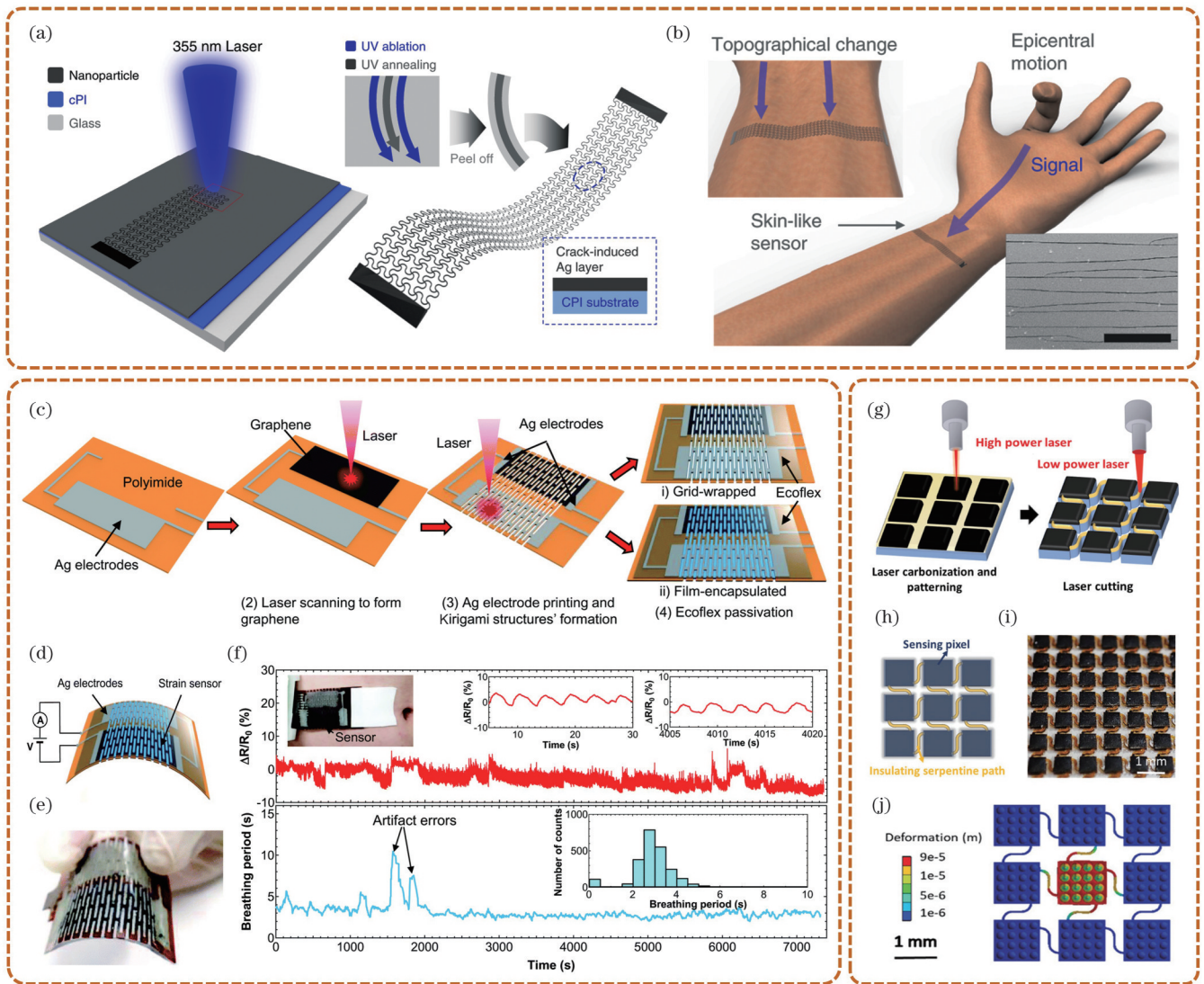


图 5 柔性物理传感器。(a)利用激光图案化和激光诱导裂纹制造高灵敏皮肤传感器的示意图^[205]；(b)测量手指震中运动的示意图，其中左上图展示了手指运动引起手腕形态变化的测量，右下图展示了传感器裂纹区域的扫描电镜图，比例尺为 $40\ \mu\text{m}$ ^[205]；(c)应变传感器的制造过程示意图，包括丝网印刷 Ag、激光直写制备石墨烯薄膜和 Kirigami 结构，以及 Ecoflex 钝化^[200]；(d)具有印刷电极的集成装置示意图^[200]；(e)弯曲状态下的装置照片^[200]；(f)上图是一名志愿者在办公室工作期间的呼吸监测结果（插图：装置固定在腹部区域的照片以及对应呼吸的阻值变化放大图），下图是从上图中提取的实时平均呼吸周期（插图：2 h 内的呼吸周期直方图）^[200]；(g)蛇形互连压阻式传感器材料阵列的激光制备工艺^[206]；(h)活性层的俯视图，包括感知像素和绝缘蛇形路径^[206]；(i)材料阵列图片^[206]；(j)蛇形互连模型底视角下的活性层变形分布^[206]

Fig. 5 Flexible physical sensors. (a) Schematic diagram of fabrication of highly sensitive skin sensor by laser-patterning and laser-induced crack generation^[205]; (b) illustration of measuring the epicentral motions of fingers, where the upper left image depicts the measurement of the topographical change of the wrist caused by the finger motions, and the lower right image shows the SEM image of the cracked region of the sensor, with a scale bar of $40\ \mu\text{m}$ ^[205]; (c) schematic of the strain sensors fabrication processes, including screen printing of Ag, laser direct writing to form graphene films and Kirigami structures, and Ecoflex passivation^[200]; (d) schematic of an integrated device with printed electrodes^[200]; (e) a device photo under bending^[200]; (f) upper image shows respiration monitoring during office work of a volunteer (insets: a photo of the device attached to the abdominal area and zoom-in of the resistance change results corresponding to breathing), and lower image shows the real-time averaged breathing period extracted from the upper image (inset: histogram of the breathing period for 2 h)^[200]; (g) laser fabrication process of the piezoresistive sensor material array with the serpentine interconnect^[206]; (h) top view of the active layer, including sensing pixels and insulating serpentine paths^[206]; (i) picture of the material array^[206]; (j) deformation distribution on active layers from the bottom view of the serpentine-interconnect model^[206]

滴的振动传感机制避免了传统弹簧式振动传感器中常见的共振现象以及摩擦起电过程中的损耗，更有利于获得均匀响应信号和持久性能。凭借本征柔软性和良

好的机械适配性，该器件可以共形贴附在曲面和人体表皮上[图 6(i)]，并对人体的不同运动强度给出合理响应值，以有效区分走路、跳跃、跑步和滑倒(信号峰值

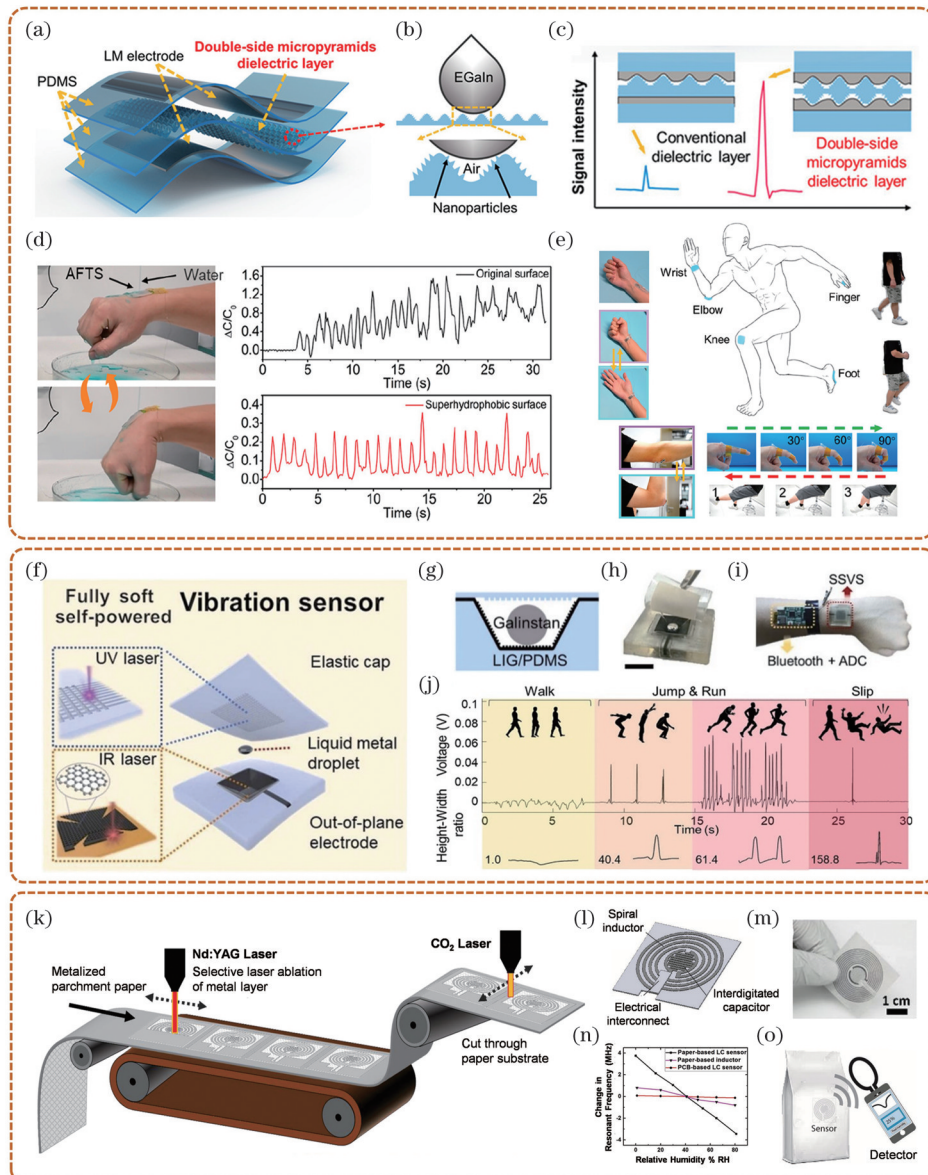


图 6 柔性物理传感器。(a) 电容式压力传感器的组装示意图^[209]；(b) LM 在激光结构化介质层上的示意图^[209]；(c) 信号强度的增强原理^[209]；(d) 将水倒在传感器上时，附着在手腕上的传感器电容曲线^[209]；(e) 可穿戴高灵敏全柔性触觉传感器，用于实时监测来自人体手腕脉搏、手掌运动、肘部弯曲、膝盖弯曲、手指弯曲以及行走和奔跑运动的机械信号^[209]；(f) 全软体自供电振动传感器的示意图，展示了其结构细节和激光辅助制造^[32]；(g) 软自供电振动传感器的截面示意图^[32]；(h) 组装后的软自供电振动传感器照片，比例尺为 1 cm^[32]；(i) 佩戴在人手臂上的无线数据采集系统和软自供电振动传感器照片^[32]；(j) 软自供电振动传感器在日常活动和紧急情况下的测量信号，所有波形均以相同放大倍数显示，展示出不同高宽比^[32]；(k) 卷对卷制造示意图^[48]；(l) 一种无电池电感电容传感器的设计概念，用于测量密封包装内的湿度水平^[48]；(m) 制造出的 3 cm × 3 cm 湿度传感器^[48]；(n) 不同传感器谐振频率随相对湿度的变化^[48]；(o) 传感器的谐振频率可以通过连接到射频 (RF) 读卡器的外部线圈进行远程测量^[48]

Fig. 6 Flexible physical sensors. (a) Schematic of assembly of the capacitive pressure sensor^[209]；(b) schematic of the LM on the laser-structured dielectric layer^[209]；(c) enhancement principle of signal intensity^[209]；(d) capacitance curve of the sensor attached on the wrist when pouring the water on the sensor^[209]；(e) wearable highly sensitive all-flexible tactile sensor for real-time monitoring of mechanical signals from human wrist pulse, palm movement, elbow bending, knee bending, finger bending, and walking and running movement^[209]；(f) schematic of the fully soft self-powered vibration sensor (SSVS) showing its structural details and laser-assisted fabrication^[32]；(g) cross-sectional schematic of SSVS^[32]；(h) photo of the assembled SSVS, with a scale bar of 1 cm^[32]；(i) photo of a wireless data acquisition system and SSVS worn on a human arm^[32]；(j) measured signals of SSVS during daily activities and emergencies, all waveforms are displayed at the same magnification showing various height-width ratios^[32]；(k) schematic illustration of roll-to-roll fabrication^[48]；(l) design concept of a battery-less inductive-capacitive (LC) sensor that measures the humidity level inside a sealed package^[48]；(m) fabricated 3 cm × 3 cm humidity sensor^[48]；(n) change in sensors resonant frequency of different sensors as a function of relative humidity (RH)^[48]；(o) the resonant frequency of the sensor can be remotely measured using an external coil connected to an RF reader^[48]

高宽比分别为 1.0、40.4、61.4、158.8) [图 6(j)], 展现出适用于健康管理 and 安全事故检测的潜力。

除了上述提及的典型接触式物理传感参量, 柔性湿度传感器凭借其湿度变化快速响应的独特特性, 在非接触测量中发挥着至关重要的作用^[216-218]。基于激光融合制造技术, 一种用于食品智能包装的柔性无线湿度传感器应运而生 [图 6(m)、(o)]。在卷对卷制造设备的辅助下, Gopalakrishnan 等^[48]通过快速激光在商用铝膜烘焙纸上原位烧蚀出电路轨迹图案, 随后利用高能激光模切形成独立传感器, 并且在激光焊接线圈与湿敏交叉电容之间形成互连结构 [图 6(k)、(l)]。基于电感-电容 (LC) 谐振电路, 该传感器的谐振频率可以反映环境湿度。激光诱导 Al_2O_3 NP 的固有湿度响应特性使得传感器灵敏度比传统光刻法制备的器件高 10 倍, 在 0~85% 的相对湿度 (RH) 范围内, 该传感器频率呈线性变化, 平均灵敏度为 $-87 \text{ kHz} \cdot \text{RH}^{-1}$ ^[48], 具有良好的可重复性和稳定性 [图 6(n)]。

5.2 柔性化学传感器

化学传感器能够通过快速检测生物标志物、代谢物、气体等化学信息揭示多种生化指标^[219]。与大多数以获取目标对象物理状态或生命体征信息为目的的柔性微纳传感器不同, 柔性化学传感器为分子水平的无创监测提供了直接方式^[220], 在人体生理信号感知、体液成分检测、环境质量监控和自供电传感系统集成等方面具有一定可行性。目前, 基于激光融合制造技术, 一系列先进的柔性微纳化学传感器已经被开发出来^[49, 221-222]。

在环境离子传感方面, Chen 等^[221]通过激光诱导调整石墨烯的结构、电导率和润湿性, 构造出多路复用的开放式微流体传感器。研究发现, 激光加工作为一种可扩展技术, 不仅可以使 PI 转化为亲水性 LIG, 用于实现开放式微流体路径和电化学传感通道, 还可以在低通量原位二次处理下将石墨烯表面由润湿态转变为近超疏水态, 用于创建通道侧壁, 以完成全 LIG 开放微流体模式 [图 7(a)]。这种对材料特性的精确控制使得器件能够沿 4 条多分叉路径将单个水样划分为 3 个离子选择电极 (分别用于 K^+ 、 NO_3^- 、 NH_4^+ 的检测, 检出限分别为 $10^{-5.01}$ 、 $10^{-5.07}$ 、 $10^{-4.89} \text{ mol/L}$), 并用于对有机磷农药 (对硫磷) 进行监测的酶促农药传感器 (检出限为 15.4 pmol/L) [图 7(c)、(d)、(e)、(f)]。此外, Chen 等^[221]还采用相同的激光合成技术制备出一种电化学微型超级电容器 [图 7(b)]。该种基于 LIG 的激光可调制方法有利于低成本实现涉及界面化学的广泛应用, 如电化学传感、能量存储、油水分离与太阳能海水淡化等。

在气体传感方面, 利用激光微纳加工可以制造多种气敏材料。其中的金属氧化物半导体作为关键气敏材料之一, 对极性气体或还原/氧化性气体尤其敏感^[223-225]。Qian 等^[222]利用激光微加工法合成了一种用

于室温下 NO_2 检测的柔性 ZnO 气体传感器 [图 7(h)], 合成步骤包括高通量激光直写 LIG 电极以及基于碳电极的激光诱导局部水热合成 ZnO [图 7(g)]。与传统 ZnO 基气体传感器不同, 该工作器件通过气敏测试展现出 p 型半导体特征, 这可能源于碳掺杂和低测试温度 ($25 \text{ }^\circ\text{C}$) 下无法形成价带电子热激发。此外, 该柔性 ZnO 气体传感器在室温下对 NO_2 的响应为 0.71%, 具有良好的稳定性 (30 d)。在温度为 $25 \text{ }^\circ\text{C}$ 、 NO_2 体积分数为 0.1% 的环境中, 器件在基底弯曲曲率于 $22.34 \sim 4.16 \text{ mm}$ 之间变化时展现出较高可重复性。然而, 此项工作对于检测空气中的 NO_2 仍存在一定局限性, 并且环境湿度也会对其响应造成影响, 需要后续研究的持续完善。

基于多激光辅助集成工艺, Lei 等^[49]成功制备出纳米晶 SnO_2 气体传感器。与热蒸发和湿化学合成等其他纳米材料制备方法相比, 此工作采用的多激光工艺具有独特优势, 其将电极制造、纳米材料组装和后续处理集成在同一道工序中, 显著提升了加工效率。该柔性气体传感器已被证明可用于 H_2 检测, 在 $320 \text{ }^\circ\text{C}$ 最佳工作温度下的传感响应值约为 $2.105 \times 10^{-4} \sim 2.500 \times 10^{-3}$ 。

在生物标志物传感方面, 可穿戴电化学传感器可以从生物液体中检测出分子水平信息, 常用于生理健康评估^[226-229]。然而, 要在复杂的生物液体中对多种标志物进行多重检测, 通常需要高密度阵列^[230], 这对低成本制造方法提出了挑战。面对这一问题, 研究人员将激光直写三维多孔石墨烯泡沫作为多路柔性电化学传感器来同时检测人体汗液中的特定生物标志物和电解质 [图 7(i)]^[37]。其中, 激光直写技术分别用于在 PDMS 基底上制备微流控通道 (引流生物液体) 和碳化 PI-多孔石墨烯电极 [图 7(j)、(k)]。所制备的电化学传感器对于汗液中的多种生物标志物具有高灵敏度和低检出限特点, 例如, 其对尿酸、多巴胺、酪氨酸、抗坏血酸的灵敏度分别为 6.49 、 6.87 、 0.94 、 $0.16 \mu\text{A} \cdot \text{L} \cdot \mu\text{mol}^{-1} \cdot \text{cm}^{-2}$, 检出限分别为 0.28 、 0.26 、 1.43 、 $11.3 \mu\text{mol/L}$ 。同时, 该电化学传感器对高嘌呤饮食后增加的汗液尿酸以及运动期间汗液电解质浓度的灵敏感知, 为无创连续监测人体痛风和水合作用状态提供了机会 [图 7(l)], 进一步监测药物摄入后汗液中的咖啡因 (CAF) 和对乙酰氨基酚 (APAP) 还可以对药物进行评估, 避免过量服用。

5.3 柔性电生理传感器

人体内的器官、组织和神经活动等均与电势有关, 通过监测生物特征电生理信号有助于发现异常生命体征。特别地, 心脏 (心电, ECG)、肌肉组织 (肌电, EMG) 和大脑 (脑电, EEG) 等相关疾病可以通过电生理传感器进行预判^[231]。近年来, 与电生理信号监测相关的可穿戴传感器已被广泛用于获取身体和认知功能, 并作为健康监测、诊断的重要基础^[232-234]。就传感

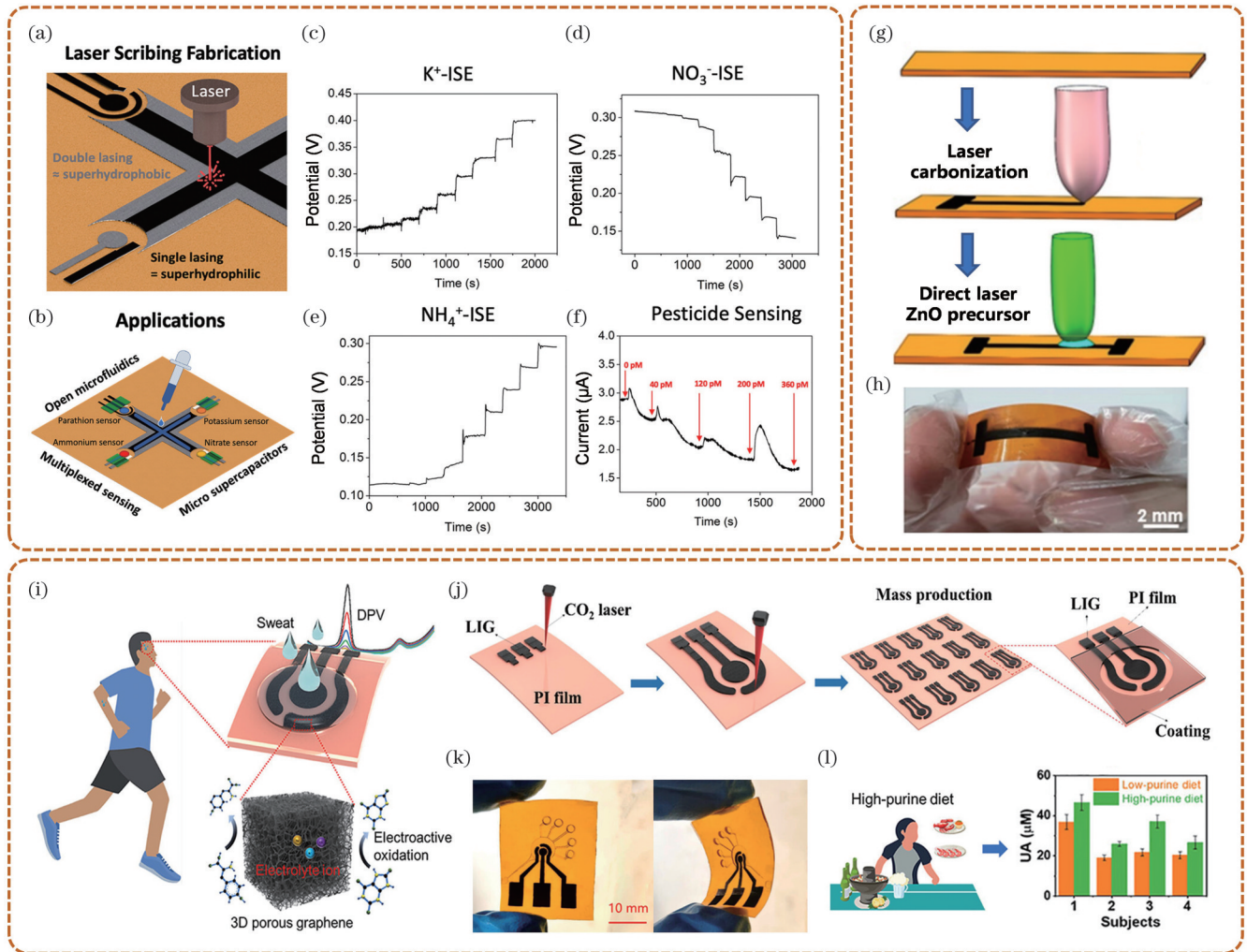


图 7 柔性化学传感器。(a)一体化开放微流控多路生物传感平台的激光制备示意图^[221]；(b)该生物传感平台用于离子和农药检测的功能化示意图^[221]；(c)(d)(e)钾离子选择电极(K^+ ISE)、硝酸盐离子选择电极(NO_3^- ISE)和铵离子选择电极(NH_4^+ ISE)在 10^{-6} ~ 10^{-2} mol/L 浓度范围内分别对 KCl、 KNO_3 和 NH_4Cl 溶液的开路电位响应^[221]；(f)酶促农药传感器对不同浓度对硫磷的电流和时间响应^[221]；(g)柔性 ZnO 气体传感器的制作过程示意图^[222]；(h)柔性 ZnO 气体传感器的照片^[222]；(i)(j)用于痛风管理和评估体内水分状况的多通道电化学传感器结构及其制造过程示意图^[37]；(k)与微流控网络集成的电化学传感器弯曲前后的光学图像^[37]；(l)高强度锻炼前，低嘌呤和高嘌呤饮食下人体汗液中尿酸水平的比较^[37]

Fig. 7 Flexible chemical sensors. (a) Laser fabrication schematic of the all in one open-microfluidics multiplex biosensing platform^[221]; (b) functionalization schematic of the biosensing platform for ion and pesticide sensing^[221]; (c)(d)(e) open circuit potential response of the potassium ion-selective electrode (K^+ ISE), nitrate ion-selective electrode (NO_3^- ISE), and ammonium ion-selective electrode (NH_4^+ ISE) to KCl, KNO_3 , and NH_4Cl solutions, respectively, within the concentration range from 10^{-6} to 10^{-2} mol/L^[221]; (f) current vs time response of an enzymatic pesticide sensor to different concentrations of parathion^[221]; (g) schematic illustration of fabrication procedure of flexible ZnO gas sensor^[222]; (h) photograph of the flexible ZnO gas sensor^[222]; (i)(j) schematics of structure and fabrication process of multiplexed electrochemical sensors for gout management and evaluation of the body's hydration status^[37]; (k) optical images of the electrochemical sensor integrated with a microfluidic network before and after bending^[37]; (l) comparison in the human sweat uric acid level under low- and high-purine diets before extensive exercise^[37]

器制造而言,激光融合加工具有高效、高质量制备功能纳米/微米级材料的技术优势,赋予了柔性电生理传感器独特、无创的感知能力,可助力定制化健康诊疗服务和面向假肢、机器人技术的可穿戴设备开发。

在柔性电生理传感中,通过皮肤贴片式可拉伸装置进行生理监测已受到广泛关注^[235-236],然而,阻碍其发展的关键问题在于如何在外部变形下保持设备性能。对此,Gandla团队^[237]基于自然启发的可变形结构

和机械隔离思路,设计了一款包括 Kirigami 图案(具有高三维面外变形能力)、蜘蛛网图案(具有结构稳定和高面积覆盖特点)和丝状蛇形图案(具有二维可拉伸性)的几何传感器[图 8(a)]。当该传感器被置于球面上时,丝状图案显示出高水平可变形性[图 8(b)]。如图 8(d)所示,它还可以作为超薄、透气和富有黏性的贴片式传感器(厚度为 250 μm 时的透水性 $> 20 g \cdot h^{-1} \cdot m^{-2}$)。传感器整体由双外层 PI 和中间层金属 Au/Ti 形成堆

叠结构[图 8(c)]。高通量激光分别用于烧蚀图案化金属薄膜和选择性刻穿金属-聚合物堆叠薄膜。整个激光制备过程简单、快速,这使得独特和坚固的几何构型可以通过一步图案化高效实现。为了验证该柔性可穿戴传感器的实际应用效果,研究人员将其用于获取各类电生理信号,如 ECG、EMG 和 EOG 信号[图 8(e)]。其中,作为试点研究,肌电传感部分被用于控制人机界面,以操作家用电器和监测精神压力。此类基于激光融合制造和新型机械结构设计的研究工作将为可穿戴智能传感器带来新机遇。

由于可拉伸电子皮肤传感器在连续监测电生理活动方面的极大促进作用^[238-240],该团队继续充分挖掘激光融合制造的可扩展优势,巧妙利用不同波长激光器的加工特点,提出了一种贴片式可拉伸大面积多通道肌电传感器阵列^[50]。如图 8(f)所示,他们首先使用纳秒紫外激光进行烧蚀加工,包括 Al 蚀刻、Al 切割和堆叠层切割,然后使用 CO₂ 激光进行 Ecoflex_PDMS-PEIE 贴片钻孔[图 8(g)]。总体而言,利用此项激光加工技术成功将功能材料与基底材料大面积转化为结构可拉伸系统,同时,对于覆盖人手臂约 20 cm 宽的大尺寸贴片器件,该技术能够以超快速度(<4 min)批量实现图案分辨率低至 50 μm 的加工产出。所制备出的贴片传感器由于可拉伸网状蛇形结构和可变形肌电电极阵列而表现出良好的共形附着能力[图 8(h)],在 10000 次循环的显著机械载荷(最大应变为 30%)下仍保持着优异机电性能[图 8(i)],并已在基于生理信号传递手势动作来控制人形机械臂的运动中实现了应用。

此外,可穿戴式柔性电生理传感器在人机界面应用中也大有前景。作为最直接反映肌肉运动信息的生物电位信号之一,EMG 常用于医学及相关研究领域的运动状态评估,同时也在向健康监测、假肢/矫形器控制、人机界面等领域扩展^[241]。近年来,基于织物的表面 EMG 传感器已成为长期可穿戴系统的研究热点^[242-244],然而,如何保持皮肤-电极接触以获得可靠的表面 EMG 信号仍是一个关键问题。摒弃染色、电镀、刺绣、针织/编织、喷墨印刷等传统工艺手段,Jeong 等^[245]介绍了一种基于 2.5 维激光切割的密织导电织物加工技术。如图 8(j)所示,为了将导电部件精确置于预设位置和形状上,利用激光减材工艺在重叠状态下切割织物。通过调节光强,可以实现同时或仅切割顶部织物。其中,高强激光束穿透两种织物切割出整体轮廓,低强激光束仅穿透顶层织物并切割出导电部分轮廓,切割后可将不需要的部分去除。该制造方法使得织物基 EMG 传感器的快速、精确、可重复、个性化加工成为可能,可以充分适配人体的不同部位。此外,研究人员还将定制传感器与意图识别算法相结合,形成了完整的智能肌肉接口,并通过手势识别证明了该表面 EMG 传感系统的有效性[图 8(k)]。结果显示,

5 名受试对象对 28 个手势识别的平均准确率高达 93.21%,出汗条件下的平均准确率可提高至 94.34%。这些结果有助于未来可穿戴式 EMG 系统在各类肌肉界面应用中的研究。

5.4 柔性多模态传感器

尽管人们已经致力于通过激光融合制造技术来提高各种柔性传感器在物理^[32,48,200,205-206,209]、化学^[37,49,221-222]、电生理^[50,237,245]参量监测等方面的性能,但这些设备往往只能对某种特定的物理或化学量实现单一感知、检测或监测,不足以解读多层次和全局性信息。因此,开发柔性多模态传感器成为了一种必然趋势。多模态传感器集成了多类感知元件,可以对多目标、多参量进行同时测量和综合分析,以获取更多相关性指标^[246],在可穿戴传感平台^[47,247]、人-机-环境交互^[46,248]中具有广阔应用前景。这里将主要展示一些激光融合制造及其在柔性多模态传感器中的典型例子。

在多功能传感系统中,丰富的信号和多参数解耦对于同时进行多模态测量至关重要,当界面上多种参数同时变化时,功能间的相互干扰会使系统无法准确响应。对此,Zhang 团队^[46]提出了一种基于全激光单步直写的双面可穿戴系统解决方案[图 9(a)],该方案既可以实现多功能传感,又可以避免多参数之间的干扰。其中,CO₂ 激光等材诱导 PI 基底改性形成多孔、高表面积 LIG,同时,参数定制化激光通过平衡图案分辨率、电导率和比表面积等特征生成影响传感性能的各种微纳结构。如图 9(b)所示,LIG 的可拉伸蛇形互连结构和轻量化特性增加了多功能系统与人体皮肤的契合度,增强了用户的实际穿戴体验。该柔性多功能传感系统允许同时测量人体电生理信号(如 ECG 和 EMG)、机械运动/物理刺激(如应变、压力、温度和接近)以及生化标志物/气体(如 Na⁺、H⁺、丙酮气体和 NO₂)的浓度[图 9(c)],并从能量收集器和能量存储单元中进行产能、储能。

虽然表皮电子设备可以无线、灵敏地检测人体健康状况,实现个性化、远程医疗保健,但其实际应用还取决于持续电源的发展。当前,一种前景性的解决方案是将高性能表皮电子传感器和信号处理电路与可伸缩能量采集器、能量存储设备、电源管理电路以及用于全自供电可穿戴电子器件的无线数据传输组件集成在一起^[249-250],然而这往往涉及到复杂的制造工艺(如光刻、沉积或蚀刻),而且器件加工过程中的高温也会破坏活性功能材料,导致柔性/弹性体聚合物基底变形。此外,大多数具有不同材料和工作原理的自供电可穿戴系统在机械变形和人体皮肤运动时存在输出功率低和信号不稳定的问题。为克服上述不足,一种基于激光诱导石墨烯泡沫的自供电可穿戴传感平台被制造出来^[47]。在加工工艺方面,该工作利用 CO₂ 激光光热转换生成三维多孔 LIG,通过无机盐涂覆和激光二次还原实现对 LIG 的原位功能化修饰,形成具有层状结构

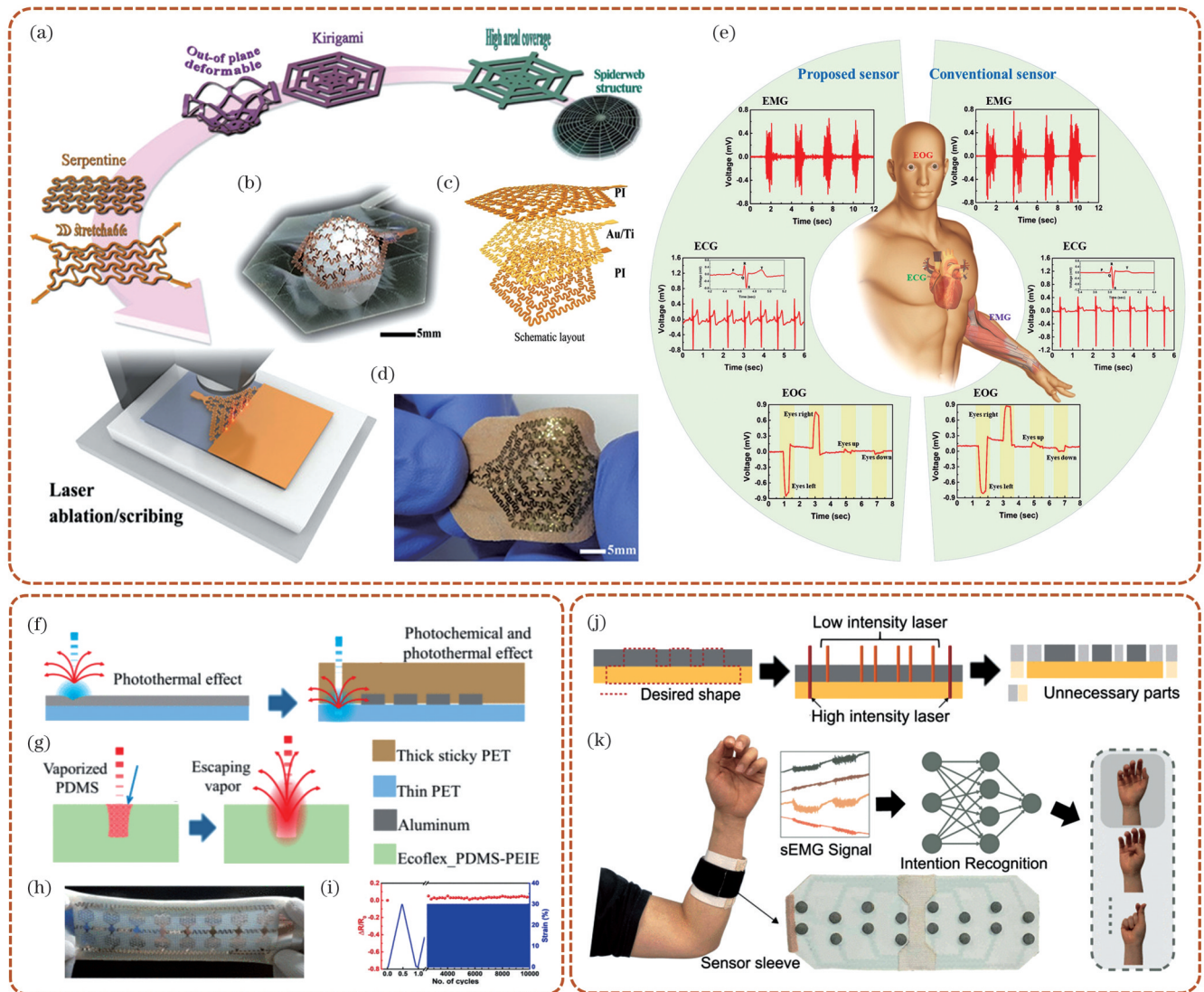


图 8 柔性电生理传感器。(a)用于电生理传感的受自然启发的 Kiri-Spider 蛇形结构设计和激光制造示意图^[237]；(b)放置在球面上的具有高度可变形性的电极图案^[237]；(c)传感器的逐层设计布局^[237]；(d)传感器附在具有黏性、透气和可拉伸性的贴片上^[237]；(e)用于测量 EMG、ECG 和 EOG 的制造电极和传统电极示意图与图形表示^[237]；(f)紫外激光烧蚀对 Al 膜进行图案化，随后切割堆叠层^[50]；(g)CO₂激光在贴片上钻孔^[50]；(h)贴片传感器阵列的光学图像，展示出对人体皮肤的柔性、可拉伸、黏性和共形贴附特点^[50]；(i)最大应变为 30% 时的循环测量^[50]；(j)2.5 维激光切割工作原理侧视图^[245]；(k)基于开发的传感器袖套和以卷积神经网络 (CNN) 为基础的意图识别算法进行手势识别^[245]

Fig. 8 Flexible electrophysiological sensors. (a) Schematic illustration of the nature-inspired Kiri-Spider serpentine structural design and laser fabrication for electrophysiological sensing^[237]；(b) electrode patterns exhibiting high levels of deformability placed over a spherical surface^[237]；(c) layout of layer-by-layer design of the sensor^[237]；(d) sensor attached to the sticky, breathable and stretchable patch^[237]；(e) schematic and graphical representation of both proposed and conventional electrodes for measuring EMG, ECG and EOG^[237]；(f) UV laser ablation to pattern Al films followed by cutting the stack layer^[50]；(g) CO₂ laser to drill the holes in the patch^[50]；(h) optical image of the patch-based sensor array exhibiting flexible, stretchable, sticky, and conformal adhesion to human skin^[50]；(i) cyclic measurements under a maximum strain of 30%^[50]；(j) side view of working principle of 2.5D laser cutting^[245]；(k) gesture recognition using developed sensor sleeve and employed convolutional neural network (CNN)-based intention recognition algorithm^[245]

或嵌入纳米晶体的复合材料,为进一步调控、优化传感性能提供可能;在自供电方面,该传感平台联合纳米发电机 (TEG)、整流器以及平面微型超级电容器实现高效收集人体机械能并将其转化为连续、稳定的电能 [图 9(d)、(f)],从而为各类可穿戴电子器件持续供电 [图 9(e)];在智能监测方面,由于该柔性可穿戴传感

器轻薄柔软、亲肤灵活、易于集成 [图 9(g)、(h)],借助无线传输技术可以实现包括脉搏、应变、温度、心电、血压和血氧等多模态生理信号的监测,并获得从人体皮肤到移动用户界面的临床相关数据,展现出其在健身安全和医疗诊断等方面的潜力。

由前述案例可以看出,柔性可穿戴监测系统对于

诊断身体状况至关重要,与此同时,它对预测病理情况也十分关键。运动传感器是柔性可穿戴监测系统的重要组成部分,然而,迄今为止,在软电子学领域,基于无疲劳软质量块的惯性运动传感器尚未得到广泛探索。为了解决这一需求并简化设备制造,研究人员提出了一种全软的 LIG-LM 一体化多功能可穿戴运动监测平台^[247],该平台同时集成了惯性、温度、湿度和呼吸传感器[图 9(i)]。其中,惯性传感器将涂有 LIG 粒子层的 LM 液滴限制在 PDMS 流体通道内,如图 9(j)所示。这不仅实现了 LM 的高度可移动,而且在保持其高导电性和机械坚固性的同时为自由移动质量体创造了振动空间,使惯性传感器具有 $6.52\% \text{ m}^{-1} \cdot \text{s}^2$ 的高灵敏度和出色的耐久性(>12500 次循环)。该多功能平台通过快速激光技术进行各功能层的图案化直写、碳化、切割,以及 PDMS 通道的表面纹理化(增强疏水性以促进液滴迁移)。此外,该平台与可编程片上系统(PSoC)集成后可作为独立系统运行,用于实时监测人体健康活动[图 9(k)]、机器人运动[图 9(l)]以及通过人机接口控制机械臂。

未来,对于表皮多功能平台的开发还将继续扩展至生化传感,以便更准确和更全面地反映健康状况,为个性化诊疗和疾病预防提供深层次信息。在这一方面,Gao 团队^[35]率先利用激光融合制造技术实现了一种集微流体汗液采样(激光减材刻蚀)、化学分子传感和多重生命体征监测(激光光热诱导碳化)为一体的柔性可穿戴传感器[图 9(m)]。具体而言,微流体模块用于动态汗液采样[图 9(n)],化学传感模块用于准确、快速检测出低浓度尿酸和络氨酸(生理浓度下的低检出限分别为 $0.74 \mu\text{mol/L}$ 和 $3.6 \mu\text{mol/L}$)[图 9(o)],多路物理传感模块用于连续监测体表温度(灵敏度为 $0.06\% \text{ } ^\circ\text{C}^{-1}$,检测限低至 $0.051 \text{ } ^\circ\text{C}$)和呼吸速率/心率(10000 次弯曲循环后的电阻保持稳定)。如图 9(q)所示,最终的多模态系统总共包含 5 层结构,且该系统可作为一次性贴片集成到柔性印刷电路板上[图 9(p)]。当被舒适地佩戴在身体不同部位时,该装置可以实时原位测量出人体运动过程中的多状态生化信息[图 9(r)],在痛风、代谢紊乱等相关疾病的无创监测方面具有潜在应用价值。

同样专注于皮肤电子开发,Ko 团队发现以往的研究大多侧重于提高设备本征性能而缺乏对佩戴传感器个体特性差异化的考虑,这种趋势将会限制设备在实际使用中执行多样化任务和适应不同环境的能力。尤其是皮肤传感器,其受到目标身体部位和用户的影响很大,因此需要进行各种设计调整,以获得最佳器件性能^[251-253]。面对修改时的整体流程初始化挑战,他们提出了一种设计-制造同步化的可定制超薄电子平台^[51],用于原位适应性操作(SOA)。如图 10(a)、(b)、(c)所示,SOA 可重写工艺基于典型的激光增、减材融合制造,为传感器、互联电路、柔性天线的灵活定制化制备、

扩展和修改提供了可能,而且该工艺可主动适应不同用户需求和相应附着位置[图 10(d)]。通过 SOA 开发出的皮肤电子能在体表实现蓝牙传输[图 10(e)],将其与各类传感元件结合可以实现皮肤状况感知(温度、紫外线、湿度)[图 10(f)]、电生理信号(ECG,EMG)追踪[图 10(g)]和虚拟手实时控制[图 10(h)]。总之,该项工作为定制化可穿戴皮肤电子产品的发展带来了福音。

柔性多模态传感系统除了用于以“人”为核心的智能监测与医疗诊断,还可以用于软体机器人交互控制。尽管软体机器人已经在复杂物体抓取上克服了传统刚性机器人所面临的长期挑战^[254],但它们在手部灵巧活动方面仍有待提高^[255-256]。因此,为软体机器人手开发传感器便成为关键一步。用于软体机器人手的传感器网络需要具备柔性和可拉伸性,以贴合柔软表面并随其移动,同时避免传感器信号受到应变影响,这就对制造成本、复杂性、定制化需求以及传感集成等提出了较大挑战。除此之外,为了避免污染,食品处理和人机交互等应用还要求传感器易于更换。为解决上述问题,Bao 团队^[248]提出一种基于紫外激光加工的柔性可拉伸多模态传感器网络,它可以与软体机器人手集成。该传感器网络的制造和集成复杂度较低,成本接近于一次性用品。研究人员通过激光烧蚀策略在低功率下进行金属导线和传感单元的图案化,在高功率下进行导线分离和基底薄膜切割[图 10(i)],由此制备出温度和接近感知模块[图 10(j)],二者的结合有助于实现人-机软接触交互。作为验证,将该多模态传感器靠近并触碰玩具娃娃的额头[图 10(k)],结果显示,其可以从触点位置感知到相应的接近和温度信号。其中,红外温度计与温度传感估计值的误差为 $0.7 \text{ } ^\circ\text{C}$,接近传感器在检测到初始接触后[图 10(l)]保持 1 kPa 左右的恒定光压。以上研究将推动软体机器人在更多场景下发挥重要作用。

过去 10 多年中,各类柔性多模态传感器已被用于人体运动追踪^[257-258]、生命体征监测^[259-261]、人机交互服务^[248]等。然而,鲜少有传感系统被报道用于弱势群体的健康观测和反馈警报。Xu 等^[33]展示了一种基于 LIG 的可穿戴多模态无线传感器系统,将柔性多模态传感片与放置在一次性尿布上的无线反馈信号处理系统进行集成,可实现对婴儿睡眠状态的持续跟踪[图 11(a)、(e)]。他们利用 LIG 作为导电电极和传感材料,分别开发了倾斜、呼吸和湿度传感器[图 11(b)、(d)]。对于倾斜传感器,其由 LIG 电极与 LM 液滴耦合而成,利用激光诱导碳化和二次处理构筑微纳尺度纹理[图 11(c)],可以克服 LIG 电极、PDMS 腔体与 LM 的强黏附性问题,增强 LM 液滴的非润湿性(接触角约为 164°),并依靠 LM 液滴的天然流动性和导电性实现可控自由移动,以此探测 18 个倾斜方向。此外,激光织构表面还同时具有超疏水和自清洁特性,这使

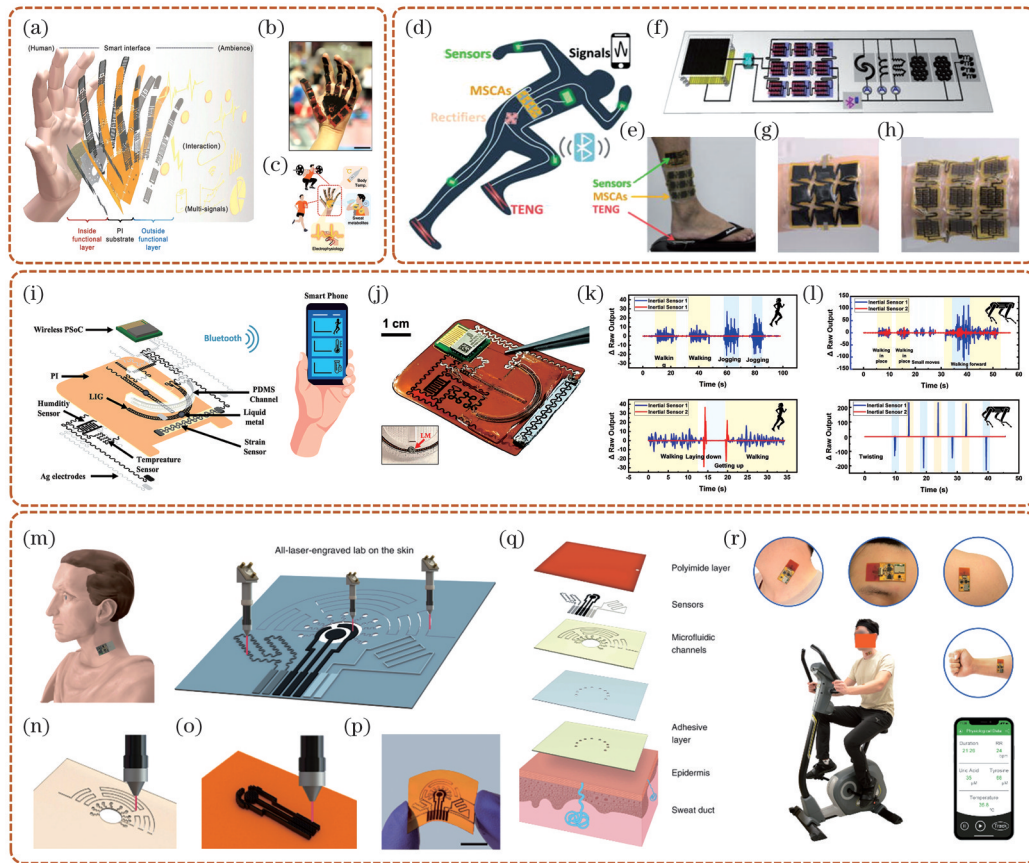


图 9 柔性多模态传感器。(a) 具有双面装置模块的可穿戴多功能系统放大示意图^[46]；(b) 健身房中的多功能系统照片，比例尺为 5 cm^[46]；(c) 人体运动过程中的系统功能示意图^[46]；(d)~(f) 基于 LIG 的自供电、无线、可穿戴传感平台的示意图和光学图像，该平台通过 TENG 从人体运动中收集能量为微型超级电容器阵列充电，从而为皮肤传感器、信号处理单元和无线数据传输组件持续供电^[47]；(g) TENG 中采用岛桥布局的可拉伸 LIG 基顶部电极的光学图像^[47]；(h) 贴附在人手腕上的可拉伸 LIG 基微型超级电容器阵列的光学图像^[47]；(i) 多功能无线平台的概念图，展示了组成该平台不同分层的爆炸视图，其中包含惯性、温度、湿度和呼吸传感器^[247]；(j) 所制造的多功能平台光学照片（插图：LM 被置于弯曲状 PDMS 通道内）^[247]；(k) 身体活动实时监测，显示传感器贴附在人体胸部时，执行如站立、行走、慢跑、躺下和起身等任务的电阻变化原始输出^[247]；(l) 机体活动实时监测，显示传感器贴附在四足机器人后背时，执行如原地行走、小幅移动、向前行走和扭转等动作的电阻变化原始输出^[247]；(m) 全激光刻写的传感器组件：微流体模块和基于 LEG 的化学和物理传感器^[35]；(n) 矢量模式激光切割制造微流体模块的示意图^[35]；(o) 光栅模式激光制造 LEG 基化学传感器的示意图^[35]；(p) 柔性实验室皮肤贴片的照片，比例尺为 1 cm^[35]；(q) 传感器的各层结构，从与表皮接触的底层到顶层^[35]；(r) 健康受试者在身体不同部位佩戴传感器贴片的照片^[35]

Fig. 9 Flexible multimodal sensors. (a) Enlarged schematic illustration of the wearable multifunctional system with double-sided device modules^[46]; (b) photograph of the multifunctional system in the gym, with a scale bar of 5 cm^[46]; (c) schematic illustration of the functions of the system during human sports^[46]; (d)–(f) schematic illustration and optical images of the LIG-based self-powered, wireless, wearable sensing platform, with the energy harvested by TENGs from kinetic human motion to charge micro-supercapacitor arrays (MSCAs) as the sustained power supply for powering on-skin sensors, signal processing units, and wireless data transmission components^[47]; (g) optical image of the stretchable LIG-based top electrode with island-bridge layout in the TENG^[47]; (h) optical image of the stretchable LIG-based MSCAs attached on a human wrist^[47]; (i) conceptual illustration of the multifunctional wireless platform showing an exploded view of the different layers composing the platform containing the inertial, temperature, humidity, and breathing sensors^[247]; (j) optical photograph of the fabricated multifunctional platform (inset: the LM placed inside the curved patterned PDMS channel)^[247]; (k) real-time physical activity monitoring showing the raw output of resistance variation of the sensor when attached to the chest of a human subject performing tasks such as standing still, walking, jogging, laying down, and getting up^[247]; (l) real-time physical activity monitoring showing the raw output of resistance variation of the sensor when attached to the back of a legged robot performing movements such as walking in place, small movement, walking forward, and twisting^[247]; (m) the sensor with entirely laser-engraved components: the microfluidic module and the LEG-based chemical and physical sensors^[35]; (n) schematic of vector-mode laser cutting for microfluidic fabrication^[35]; (o) schematic of raster-mode laser for LEG-based chemical sensors fabrication^[35]; (p) photograph of a flexible lab-on-skin patch, with a scale bar of 1 cm^[35]; (q) layers of the sensor, from the bottom layer in contact with epidermis to the top layer^[35]; (r) photographs of a healthy subject wearing the sensor patch at different body parts^[35]

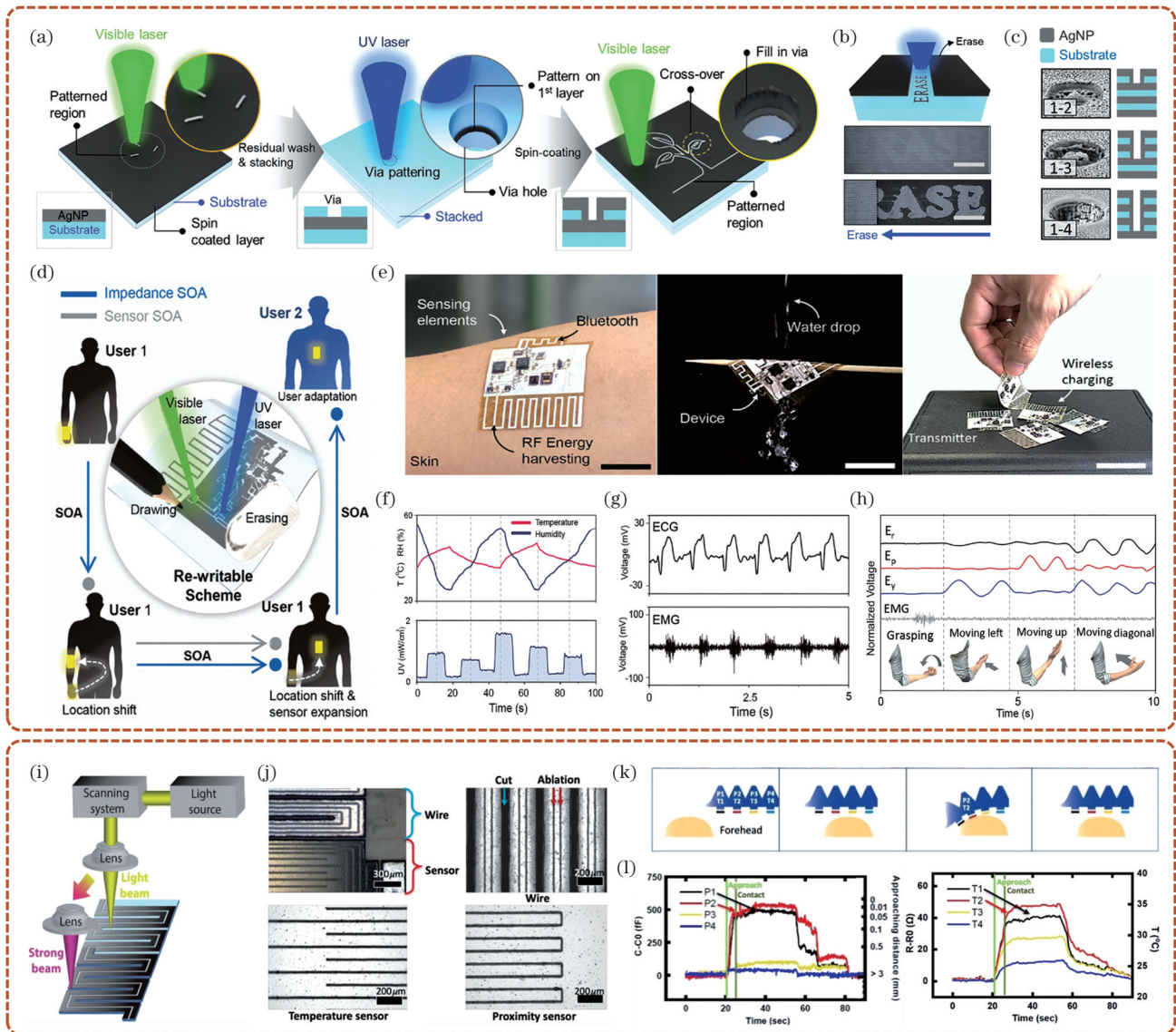


图 10 柔性多模态传感器。(a) 第一层(堆叠和形成垂直互连通道)和第二层的绘制示意图^[51]; (b) 擦除顶层电极的示意图, 附带光学图像的比例尺为 $200\ \mu\text{m}$ ^[51]; (c) 四层器件可控过孔的扫描电镜图和相应图示, 以及三层电路系统选择性过孔控制的演示^[51]; (d) 该装置通过阻抗和传感器 SOA 主动适应各种用户需求和相应附着位置, SOA 基于激光重写金属纳米颗粒^[51]; (e) 开发的皮肤电子装置图, 包括具有皮肤能量传输能力的各种传感元件, 比例尺分别为 15、15、20 mm^[51]; (f) 测量与皮肤状况相关的各种因素(实时温度、紫外线和湿度)^[51]; (g) 测量 ECG 和 EMG 信号^[51]; (h) 实时测量与虚拟手控制相关的陀螺仪和肌电信号^[51]; (i) 激光烧蚀策略示意图, 使用低功率激光图案化金属迹线, 使用更高功率激光切割 PET 薄膜^[248]; (j) 传感器和导线的显微图, 显示出烧蚀的 Al 传感器(红色)和切断的互连导线(青色)^[248]; (k) 软手指接近并轻轻触摸玩具娃娃额头时的相应传感器触点示意图^[248]; (l) 相应的接近度和温度信号图(标定数据位于右纵轴)^[248]

Fig. 10 Flexible multimodal sensors. (a) Schematic illustration of drawing of the first layer (stacking and vertical interconnect access (VIA) formation) and the second layer^[51]; (b) illustration of erasing the top layer electrode with accompanying optical images with a scale bar of $200\ \mu\text{m}$ ^[51]; (c) SEM images and corresponding illustration of the controlled VIA of four-layer device and the demonstration of the selective VIA control of the three-layer circuit system^[51]; (d) the device is actively adapted to the various user demands and corresponding attachment locations through impedance and sensor SOA, SOA is based on the laser rewriting of metal nanoparticles^[51]; (e) images of the developed skin electronic device including various sensing elements with on-skin power transferring ability, with scale bars of 15, 15, and 20 mm, respectively^[51]; (f) measuring of various factors that relates to skin conditions (real-time temperature, UV and humidity)^[51]; (g) measuring of ECG and EMG signals; (h) measuring of gyroscopic and EMG signals that relates to virtual hand control in real-time^[51]; (i) illustration of laser ablation strategy, using low power laser to pattern the metal traces and higher power laser to cut the PET film^[248]; (j) microscopic images of sensors and wires showing ablated Al sensors (red) and cut interconnect wires (cyan)^[248]; (k) schematic of corresponding sensor contacts of a soft finger approaching and gently touching a doll's forehead^[248]; (l) plots of corresponding proximity and temperature signals (calibrated data on the right vertical axis)^[248]

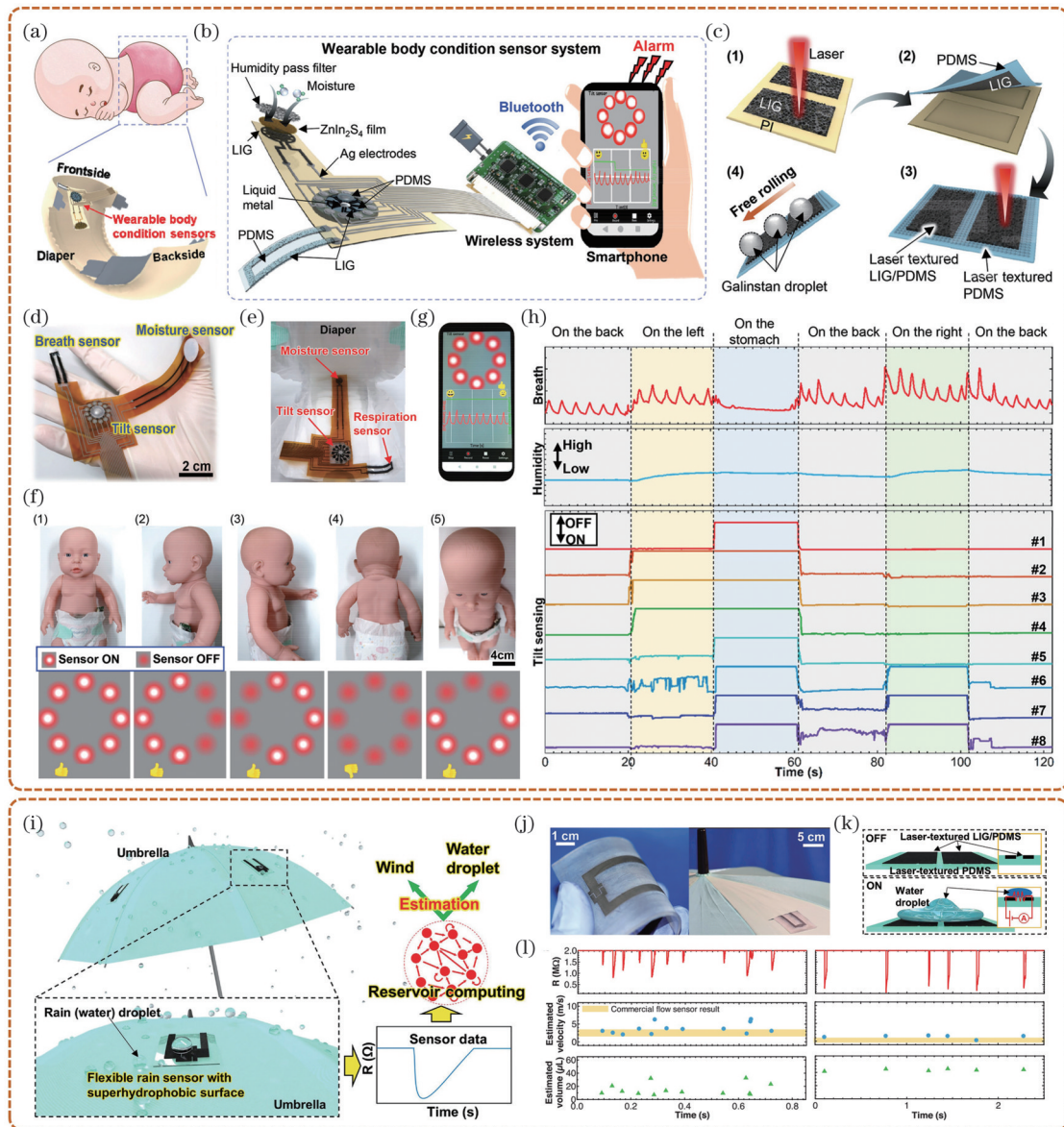


图 11 柔性多模态传感器。(a) 贴附在一次性尿布上的可穿戴传感器系统示意图^[33]；(b) 集成倾斜、呼吸和湿度传感器的可穿戴体征传感器系统示意图，多通道信号通过蓝牙无线传输到智能手机界面，智能手机可以在特定条件下发出警报^[33]；(c) 对 LM 液滴非黏附的 LIG 基软基底制备工艺示意图^[33]；(d) 制造的多模态柔性传感片照片^[33]；(e) 贴附在尿布上的多模态柔性传感器照片^[33]；(f) 从智能手机中提取的穿戴无线集成倾斜传感器的人工婴儿模型在不同体位时的照片和结果，包括仰卧(1)、右侧卧(2)、左侧卧(3)、俯卧(4)和站立姿势(5)^[33]；(g) 智能手机上的无线监测结果^[33]；(h) 躺在床垫上的成年人的无线实时监测结果^[33]；(i) 配备储存计算处理的柔性雨水传感器系统示意图^[262]；(j) 柔性雨水传感器和贴附在雨伞上的传感器照片^[262]；(k) 有、无水滴时柔性雨水传感器的传感机制^[262]；(l) 在自然风速为 $1.5\sim 3.5$ 、 $0\sim 10\text{ m}\cdot\text{s}^{-1}$ 的环境中，传感器的电阻变化、估算风速以及估算体积^[262]

Fig. 11 Flexible multimodal sensors. (a) Schematic of the wearable sensor system attached onto a disposable diaper^[33]; (b) schematic of a wearable body condition sensor system integrated with tilt, breath, and moisture sensors, multiple channel signals are wirelessly transmitted to a smartphone interface via Bluetooth, the smartphone can generate an alarm under certain conditions^[33]; (c) schematic of the fabrication process for the non-adhesive LIG-based soft substrate to an LM droplet^[33]; (d) photo of the fabricated multimodal flexible sensor sheet^[33]; (e) photo of multimodal flexible sensors attached onto a diaper^[33]; (f) photos and results extracted from the smartphone of an artificial baby model wearing a wireless integrated tilt sensor for various body positions, including sleeping on the back (1), right side (2), left side (3), stomach (4), and standing posture (5)^[33]; (g) wireless monitoring results on a smartphone^[33]; (h) wireless real-time monitoring results measured from an adult lying on a mattress^[33]; (i) schematic of the flexible rain sensor system with reservoir computing (RC) processing^[262]; (j) photo of the flexible rain sensor and the sensor attached to an umbrella^[262]; (k) sensing mechanism of flexible rain sensor with and without water droplets^[262]; (l) resistance change of the sensor, estimated wind velocity, and estimated volume in an ambient environment with natural wind flow in the range of $1.5\sim 3.5$, and $0\sim 10\text{ m}\cdot\text{s}^{-1}$ ^[262]

得可穿戴传感器即使在高湿环境中也能保持良好性能。对于呼吸传感器,将 PDMS 前驱液渗透至多孔 LIG 中形成无缝融合,可用于对皮肤应变的长期灵敏感知(经历 10000 次重复拉伸-释放后无电阻漂移现象),从而实现对婴儿呼吸速率的监测。对于湿度传感器,采用堆叠 ZnIn₂S₄ 纳米片作为敏感层、LIG 作为指叉电极共同促进水蒸气的吸收和解吸(当相对湿度由 30% 变化至 80% 时,电信号输出均十分稳定),传感器上方覆有一层防潮膜,可以避免划伤、污染以及人体与 ZnIn₂S₄ 膜直接接触。综上,结合多功能激光融合制造技术的环保、高效加工优势和有源传感材料层对物化参量变化的灵敏捕捉,将该柔性微纳传感系统集成到纸尿裤上,可以实时跟踪婴儿身体状态和尿布润湿情况[图 11(f)]。从该系统中获得的 10 通道信号可以通过蓝牙无线传输到用户友好和配备报警功能的智能手机界面[图 11(g)],以便在婴儿出现俯卧睡姿、呼吸停止或尿布高湿时及时响应反馈[图 11(h)]。总之,该柔性多模态无线传感器系统有助于加强护理人员与弱势群体(如婴儿、老年人和残障人士)之间的联系。在未来的研究中还可以考虑引入额外的传感模块,以全面跟踪皮肤温度、心率/脉搏、血氧以及其他生命体征。

在面向大自然的柔性多模态传感器中,一个典型的例子是 Takei 团队^[262]为监测实时降雨量和风速而开发的轻量雨水传感器[图 11(i)、(j)]。他们采用与 Xu 等^[33]类似的制造思路:通过激光等材碳化形成 LIG,通过激光减材织构在 LIG/PDMS 表面加工出微纳纹理。当雨水与两端导电电极接触时,形成闭合通路($< 2 \text{ M}\Omega$),随后水滴在微纳结构的超疏水作用下逐渐向外扩散,最终恢复无水的开路状态[图 11(k)]。此过程可以检测到电信号变化,并从中识别出雨水的接触动态行为(如表面停留、撞击、滑动、反弹或分裂)以及隐含的风速信息。此外,不同体积的水滴也可以反映出不同的电阻值变化。研究发现,电路导通时长与雨滴的最大半径具有良好的正相关性。受 LIG 电极间隙的限制,该工作能够精确测量到的最小水量约为 $5 \mu\text{L}$,适用于大降雨量检测。这种小巧灵活的柔性雨水传感器通过机器学习算法进行数据分析:当传感器检测到因降雨和风力条件变化导致电阻发生变化时,会将其记录为时间序列数据,利用这些数据训练机器学习算法,就可以实时输出降雨量和风速信息。如图 11(l)所示,在 $1.5 \sim 3.5 \text{ m}\cdot\text{s}^{-1}$ 的风速范围内,由传感器原始阻值数据集可以估算出降雨体积和风速。此多任务传感系统制造成本低,可轻松固定在屋顶、车辆和雨伞等表面上,从长远来看,有助于促进智能物联网社会的创新发展。

6 总结与展望

激光融合制造涵盖了光学工程、材料科学、机械制造等多学科内容,以多脉冲、多波长激光为工具,充分

集成增材、等材、减材多形式加工特点,将敏感单元的高效沉积、材料介质的诱导改性与微纳结构的精密制备融为一体,为实现高性能柔性微纳传感器提供了有效解决方案。相比于传统微纳复合加工方法,激光融合制造在以下方面具有显著优势:1) 多机制协同作用——充分结合激光加工过程中主要涉及的“热效应”与“冷加工”效应,诱导材料发生汽化、烧蚀、热膨胀、熔融凝固、反应改性、去除剥离、等离子化等现象,同时伴随着光热、光电、光化学与光机械效应;2) 多尺度制造集成——通过激光增材烧结、等材改性与减材蚀刻实现毫米、微米和纳米级跨尺度精密结构的“控形”与“控性”;3) 多材料体系兼容——利用物质对不同波长激光的吸收特性差异,实现对金属、碳基、陶瓷、聚合物等材料的选择性微纳加工。此外,激光融合制造还具有灵活可控、环境友好、加工高效、成本较低等特点,有效克服了传统工艺中存在的自由度低、流程复杂、低产低效与设备昂贵等难题。

虽然激光融合制造正在不断丰富和拓宽柔性微纳传感器的加工渠道,然而,在面向实际应用场景时,其发展仍然存在诸多挑战。首先,尽管激光融合制造在微纳加工精度方面已经取得较大突破,但精度的进一步提高受到光学衍射极限的限制,从而在一定程度上限制了该技术在高密度、高集成度器件制造方面的应用。其次,传统激光加工主要通过点扫描模式工作,对于复杂结构的制备通常需要几小时甚至更长时间,极大地降低了产率,无法满足大面积或批量化加工需求。对此,可以考虑采用微透镜、多光束干涉法、多焦点并行加工等技术优化激光扫描工艺。此外,目标材料的多样性也是激光融合制造在多模态处理方面的难题。由于不同材料需要适配不同的激光波长与加工形式,因此,在实现材料切换和工艺过渡上还需要开展更为广泛的材料特性研究,为不同材料的激光融合微纳制造提供依据,并通过参数优化,实现多材料体系的高质量加工,从而推动新型柔性微纳器件的开发。最后,在器件应用方面,由于激光融合制造具有一体化加工多功能集成传感器的潜力,因此,克服不同传感单元之间的信号串扰也是器件在设计与制造过程中面临的挑战。

总之,激光融合制造的未来发展势必会加速柔性微纳传感器的创新与迭代,开辟柔性微纳制造新路径,拓展激光加工应用新场景。

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Hybrid Laser Manufacturing and Applications in Flexible Micro-Nano Sensors (Invited)

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Abstract

Significance With the increasing demands of internet-of-things and big data, flexible electronics have become a key technology. Among them, flexible micro-nano sensors, as an important part of flexible electronics, have revolutionized the physical form of conventional rigid devices. It has significantly facilitated the interconnections among human beings, machines, and environment,

serving as a vital role for the advancement of intelligent electronics. For instance, embedding flexible micro-nano sensors in smart skins renders sensitive detection of external pressure and deformation, making them applicable in robotics and bionic hands. In biosensing applications, these sensors facilitate real-time monitoring of the internal micro-environment, drug release, and cellular activities. When applied in hand motion tracking and tactile feedback, they contribute to enhancing virtual reality interactions. It is envisioned that the emerging development of flexible micro-nano sensors will enable a new era of transformation within the industry.

Currently, a variety of commercial micro-nano manufacturing methods have been widely applied in micro-nano devices, including physical/chemical vapor deposition, photolithography, and nano-imprinting. However, the fabrication of multifunctional flexible micro-nano sensors often involves the combination of multiple manufacturing methods to achieve various tasks like sensitive material deposition, patterning, as well as generation of micro-nano structures. With the evolution of flexible micro-nano sensors towards miniaturization, integration, intelligence, and customization, the higher technical requirements are posed for the efficient multifunctional preparation of sensitive materials and the controllable fabrication of micro-nano structures.

Among various technologies available, hybrid laser fabrication based on laser additive, formative, and subtractive manufacturing, along with their combined processing modes, meets the heterogeneous requirements of multifunctional flexible micro-nano sensors in terms of multiple scales, dimensions, and materials. Leveraging its rich reaction mechanisms, flexible and controllable regulation, high-precision processing, and multi-material compatibility, it breaks through the limitations of traditional manufacturing technologies in multitasking, multithreading, and multifunctional combined processing. Based on laser and matter interactions, hybrid laser fabrication realizes cross-scale shape control and property control, which opens up a new path towards the integrated structure-material-function manufacturing of various flexible micro-nano sensors.

Progress Several published review articles on “laser fabrication of flexible micro-nano sensors” are available, which mainly elaborate on laser synthesis of micro-nano materials and laser processing of micro-nano structures. This paper focuses on hybrid laser fabrication and discusses its application strategies in the realization of flexible micro-nano sensors from a global perspective. It sequentially introduces three laser-based manufacturing methods, including additive, formative, and subtractive fabrication. The processing mechanisms and typical target materials involved are discussed. The paper highlights the technical advantages and applications of hybrid laser fabrication in flexible micro-nano sensors (Fig. 1).

In particular, based on different processing strategies of hybrid laser fabrication: (1) Laser additive manufacturing utilizes laser as a localized energy source to heat and melt nano-precursors, which accumulates layer by layer after sintering to form functional structures. Examples include laser reduction sintering of metal or metal oxide nano-inks such as copper, silver, and nickel (Fig. 2). (2) Laser formative manufacturing refers to laser-induced interfacial reactions used to change the physical or chemical properties of materials, while almost maintaining their initial volume. This is typically used to regulate the conductivity or functionalize the properties of polymers (Fig. 3). (3) Laser subtractive manufacturing mainly achieves pyrolysis, ablation, patterning, and micro-nano texturing of materials. For example, it is applied to enhance the performance of pressure sensors and fabricate high-resolution interconnect circuits (Fig. 4). Rationally combining these three laser processing strategies makes it possible to deposit nano-materials, physicochemically modify sensitive media, and pattern and precisely form micro-nano structures in multifunctional devices. This makes it feasible for the multifunctional integration and versatile manufacturing of flexible micro-nano sensors, making it a potential alternative to traditional manufacturing methods.

Subsequently, this paper discusses some typical applications of hybrid laser fabrication in flexible physical, chemical, and electrophysiological sensors in recent years, as well as flexible multi-modal sensor systems. It comprehensively demonstrates a wide range of multifunctional applications in the fields of wearable healthcare, human-machine interactions, and environmental monitoring.

Conclusions and Prospects Hybrid laser fabrication involves multiple disciplines such as optical engineering, materials science, and mechanical manufacturing. Utilizing multi-pulse and multi-wavelength laser manufacturing systems, it judiciously integrates the characteristics of additive, formative, and subtractive processing, allowing efficient deposition of sensitive materials, modification of material properties, and precise preparation of micro-nano structures. This integration provides a robust solution for realizing high-performance flexible micro-nano sensors, overcoming the technical challenges of traditional methods. Nevertheless, there are still a couple of challenges to address for practical applications. First, the further improvement of precision is restricted by the optical diffraction limit, which hinders the manufacturing of high-density and highly integrated devices. Second, traditional laser processing mainly works through the point scanning mode, and the preparation of complex structures usually takes several hours or even longer, which greatly reduces the yield and cannot meet the needs of large-area or mass-processing. In addition, the diversity of target materials has posed a challenge for hybrid laser fabrication in relation to multimodal processing. Finally, in terms of device applications, overcoming signal crosstalk among different sensing units is a key issue in the design and fabrication of devices, given the potential of hybrid laser fabrication for the integrated processing of multifunctional sensors. In conclusion, hybrid laser fabrication is envisioned to accelerate the innovation of flexible micro-nano sensors and expand the application scenarios of laser processing.

Key words hybrid laser fabrication; laser-matter interactions; micro and nano-fabrication; flexible electronics; flexible micro-nano sensors