新型能源器件的激光微纳加工研究进展

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摘要 随着科学技术的不断发展，新型能量转化和存储器件的研究受到了科学工作者的广泛关注，有望减小人类社会对化石燃料的依赖，构建全球能源新格局。激光具有能量密度高、空间分辨率高、可定制性强等特点，在先进功能材料的开发和新型能源器件的微纳结构构建方面具有独特的作用。概述了激光在新型能源器件和相关先进材料领域的研究进展，其中新型能源器件主要包括超级电容器、可充电电池、太阳能电池、水汽自发发电器件等；先进材料领域的研究进展涉及器件电极的激光微纳加工、材料的激光改性和功能化、器件结构的激光微结构构建、柔性能源器件制备等。最后，对激光在新型能源器件领域的相关研究进行了总结和展望。

关键词 激光技术；能源器件；微纳加工；能量转化和存储；先进材料

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1 引言

由于不断加剧的传统能源危机和环境污染问题，新型能源器件一直是科学工作者广泛关注的研究热点。虽然已经开发了超级电容器[1-2]、锂离子电池[3-4]、太阳能电池[5-6]、自发发电器件[7-8]等多种能源器件，但较低的能量密度、繁琐的制备工艺、单一的结构及较差的力学性能都严重限制了其在实际场景中的应用[9-10]。近年来先进功能材料和纳米技术的发展不仅为新型能源器件带来了诸多可能，也对材料和器件的设计与加工工艺提出了更高的要求与挑战。

对能源器件而言，材料的本征性质、界面的表面形貌、微观结构设计、器件的加工和集成工艺都会显著影响性能[11]。传统的机械微加工和物理化学改性方法存在工艺复杂、难以加工微纳米器件、无法对材料性质或表面形貌进行局部精准调控等问题。激光加工的峰值能量密度高、热影响区小、材料适用性广，因此可以在多种材料表面加工出特定的微结构或调控表面性质，常被用于提高能源器件的能量密度。同时，激光加工具有空间分辨率高、可定制性强的特点，不仅工艺简洁高效，而且能够对材料局部进行精准调控和改性，更有利于器件的微型化和集成，因而在先进材料和器件的精确加工领域具有巨大的研究价值和广泛的应用前景[12-15]。

本文综述了近年来激光技术在新型能量转化和存储器件领域的研究进展。首先，介绍了提高超级电容器能量密度所需解决的问题，激光加工技术在超级电容器的制备和改性方面的应用与优势；其次，介绍脉冲激光沉积技术、激光热解和刻蚀工艺在可充电金属离子电池领域应用的研究进展；然后，从太阳能电池、水汽自发发电器件等新型能量转化器件的原理和挑战出发，介绍激光技术在多种新型能源领域应用的优势和典型范例，并阐述了激光技术在柔性能源器件领域的进展；最后，总结了激光技术在新型能源器件领域应用的发展前景和趋势。

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2 超级电容器

随着电子器件的微型化，具有更高功率密度、更快充放电速率、更高容量保持率、更长使用寿命的超级电容器也受到了越来越多的关注[16-17]。为了适应高集成度、可穿戴性、可延展性等实际应用需求，超级电容器呈现出小型化、柔性化、高度定制化的发展趋势[18]。激光加工具有峰值强度高、定制化程度高、材料实用性广等特点，其极高的峰值功率可以发生瞬态局部过热和快速自淬火，可以在辐照的区域形成结构缺陷和亚稳相，因此激光加工在超级电容器微纳加工领域具有广泛的应用[19-20]。

传统双电层电容器能量的储存和释放主要依靠电解质离子在电极处的物理吸附和脱附，表面主导的储能过程虽然使得电容器具有超长的使用寿命，但受限于电极材料的有效表面积，较低的能量密度也阻碍了其广泛应用[18]。激光超高的峰值功率密度可以在局部的作用区域内与材料发生强烈的相互作用，从而能够精细地调控电极表面的微结构，为双电层电容器能量密度的提升提供了新的途径。

以激光诱导石墨烯生长为例，目前已经开发了多种基于激光的石墨烯加工技术[14]。激光诱导的化学气相沉积方法利用激光加工峰值功率高的特点，在碳源氛围下使用激光照射镍箔，可以在焦点局部产生高温，去除激光后温度迅速下降，实现在激光照射到的镍箔表面生长石墨烯的目的。这比传统的化学气相沉积方法快 3 个数量级，并且能够实现图案化生长[21-22]。更简单的、激光诱导的外延生长技术使用激光，直接在目标衬底(如聚合物或碳化硅等固态碳源)上图案化生长石墨烯。当激光照射目标衬底时，受辐照的区域温度急剧升高，引起目标衬底的热解，例如硅(Si)原子热解后从碳化硅表面脱离，而碳(C)原子重新排列后在激光辐照的区域形成石墨烯。与化学气相沉积技术相比，激光诱导的外延生长技术无需真空室和氛围保护，可以简便地进行图案化生长[23-24]。除此之外，使用激光将氧化石墨烯(GO)还原为还原氧化石墨烯(rGO)也是广泛采用的加工技术。激光辐照会在 GO 表面产生局部高温，从而在 GO 结构中产生局部化学、物理反应，例如激光照射的区域会引起 GO 表面官能团的分解，碳氧键断裂的同时碳原子会与周围的原子、化合物形成新的化学键，最终被还原为 rGO[25-26]。

在这方面，Lin 等[27]使用激光诱导的外延生长技术在商用聚合物薄膜表面制备了三维多孔的石墨烯电极，如图 1(a)所示。并通过激光功率调控了孔隙率、碳化程度等参数，最终制备的石墨烯电极的比表面积为 340 $m^2 \cdot g^{-1}$，孔径小于 9 nm，电导率为 25 $S \cdot cm^{-1}$，如图 1(b)所示。得益于电极的高电导率、高表面积和褶皱微结构，在聚合物薄膜上原位制备的电容器的比电容为 120 $F \cdot g^{-1}$，在 20 $mV \cdot s^{-1}$ 和 10000 $mV \cdot s^{-1}$ 的扫描速度下，单位面积电容分别可达到 4 $mF \cdot cm^{-2}$ 和 1 $mF \cdot cm^{-2}$，如图 1(c)所示，并且在水性电解质和离子液体电解质中循环 9000 和 7000 次后下降的电容可忽略不计。除此之外，还可以通过激光加工诱导产生石墨烯纤维[28]、微米级沟槽[29]、空间结构[30]等实现更大的比表面积。另一方面，El-Kady 等[31-32]使用标准 DVD 光驱驱动器激光将 GO 还原为具有高比表面积和高电导率的石墨烯电极，所制备的电容器不仅具有高能量密度而且具有很好的柔韧性和稳定性，并实现了高密度集成，如图 1(d)～(f)所示。Liang 等[33]则使用激光在 GO 纤维表面原位还原出 rGO 电极，所制备的电容器不仅保留了纤维的柔韧性和稳定性，并能够在一根纤维上进行电容器的高密度集成，如图 1(g)～(i)所示，并且可以编织到纺织品中构建可穿戴型储能器件。

提高能量密度的第 2 种途径是开发基于赝电容的超级电容器。赝电容电容器的储能能力主要由电极处可逆的法拉第过程决定[34]。赝电容电容器的性能主要受限于氧化还原反应过程中较差的离子、电子传导性和电容器使用寿命[11]。激光处理可以将活性材料或杂原子掺杂入电极材料中，以提高电学性能。Clerici 等[35]通过对 MoS_2 浸润的薄膜进行激光直写(DLW)处理，制备了 MoS_2 修饰的多孔石墨烯电极，如图 2(a)所示。MoS_2 的引入使得超级电容器能够以赝电容的形式储能，最终制备了具有更高输出功率的混合型电容器，如图 2(b)所示。类似的，Ye 等[36]则通过激光辐照将多种金属纳米粒子嵌入到石墨烯材料中，来提高电极电导率，如图 2(c)、(d)所示。除此之外，还可以将 Au[37]、Fe_3O_4[38-39]、RuO_2[40]等纳米材料通过激光加工掺杂到电容器电极中，以获得更好的性能。而在加速离子扩散方面，使用激光干涉在电极表面加工出周期性微沟槽结构[41]和掺杂碳纳

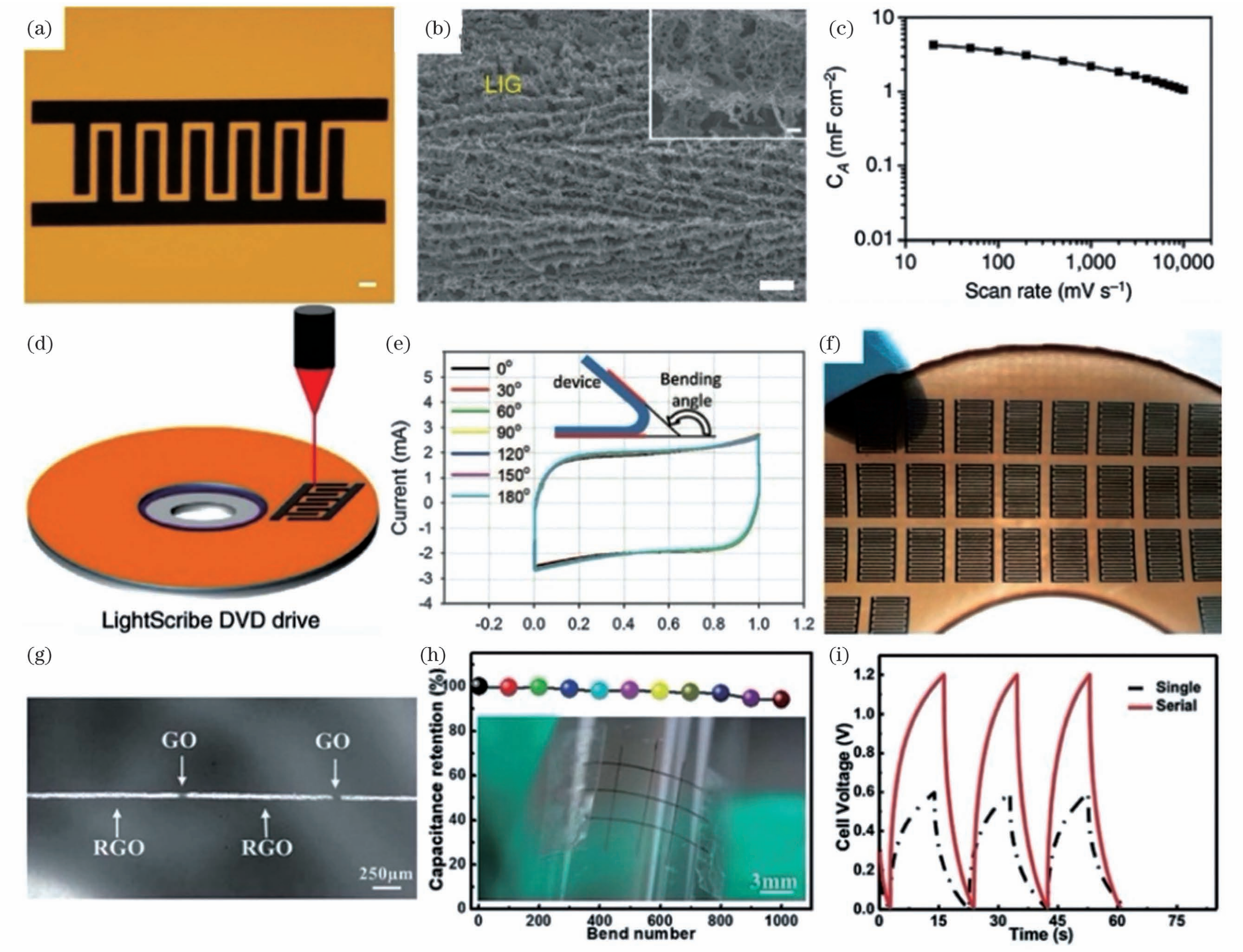

图 1 激光加工双电层超级电容器。(a)激光在聚合物薄膜表面诱导产生石墨烯电极[27];(b)多孔石墨烯电极的扫描电子显微镜(SEM)图像[27];(c)不同扫描速度下电容器的比电容[27];(d)使用标准 DVD 驱动器在 GO 薄膜上原位还原出石墨烯电极[31];(e) GO 薄膜电容器的弯曲性能[31];(f) GO 薄膜电容器的高密度集成[32];(g)使用激光在 GO 纤维上还原出 rGO 电极[33];(h) 纤维电容器在不同弯曲状态下的容量保持率[33];(i) 纤维电容器在不同弯曲状态下的串并联性能[33]

Fig. 1 Laser processing of double-layer supercapacitors. (a) Laser induced graphene electrodes on the surface of polymer films; (b) scanning electron microscope (SEM) image of porous graphene electrodes[27]; (c) specific capacitance of capacitors at different sweep speeds[27]; (d) *in-situ* preparation of graphene electrodes on GO films using standard DVD drivers[31]; (e) bending performance of GO film capacitor[31]; (f) high density integration of GO film capacitors[32]; (g) reduced rGO electrodes on GO fibers using laser[33]; (h) capacity retention of fiber capacitors at different bending states[33]; (i) series parallel performance of fiber capacitors at different bending states[33]

米管[42],如图 2(e)、(f)所示,都可以获得更大的比表面积,增强氧化还原反应,从而获得更高的能量密度和更好的循环稳定性。

3 可充电电池

电动汽车和智能电网的发展也对电池的能量密度和安全性提出了更高的要求。传统的锂离子电池需要在电极处发生氧化还原反应,而缓慢的反应动力学限制了锂电池的输出功率,充放电过程中电极的膨胀也影响锂电池的寿命和安全性[43-44]。如何提高电极的接触面积、降低电子和离子的传输距离、提高电子和离子的电导率、减小锂离子嵌入和脱出过程中的体积变化也成为了研究的重点。激光加工策略可以精细地调控电极的微观结构、构建复合材料,解决上述问题。

脉冲激光沉积(PLD)可以将广泛的物质沉积为

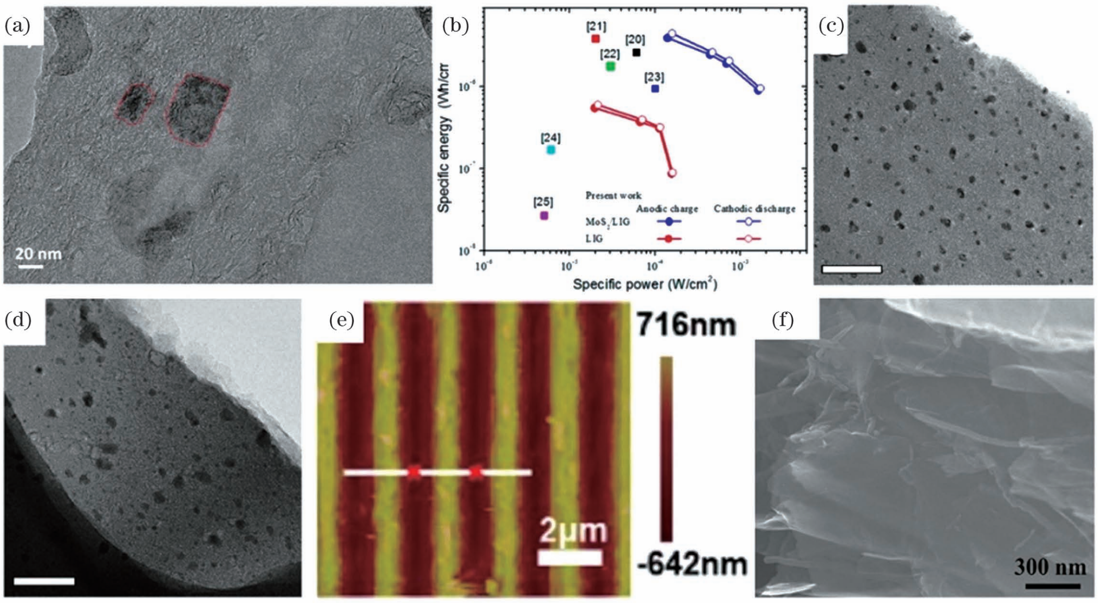

图 2 激光加工赝电容超级电容器。(a)MoS_2 修饰的多孔石墨烯电极的透射电子显微镜(TEM)图像[35];(b) MoS_2 修饰的赝电容超级电容器与未被修饰的超级电容器的性能比较[35];(c) 掺杂有 Co 纳米粒子的石墨烯电极的 SEM 图像[36];(d) 掺杂有 Fe 纳米粒子的石墨烯电极的 SEM 图像[36];(e) 激光加工在电极表面制备周期性微沟槽结构[41];(f) 激光加工在电极表面掺杂碳纳米管[42]

Fig. 2 Laser processing of pseudocapacitor supercapacitors. (a) Transmission electron microscopy (TEM) image of MoS_2-modified porous graphene electrode[35]; (b) performance of MoS_2-modified pseudocapacitor supercapacitors compared with unmodified supercapacitors[35]; (c) SEM image of graphene electrodes doped with Co nanoparticles[36]; (d) SEM image of graphene electrodes doped with Fe nanoparticles[36]; (e) fabrication of periodic micro grooves on electrode surface by laser processing[41]; (f) doping carbon nanotubes on electrode surface by laser processing[42]

具有纳米级结构的薄膜,因此常被用于电池电极制备。使用 PLD 制备的硅薄膜[45]、Fe_2O_3 薄膜[46]、钛酸钠薄膜[47]、NiO 薄膜[48]等具有纳米级晶体结构中,Fe_2O_3 电极如图 3(a)所示,与宏观尺寸的电极材料相比,可以暴露出更多的活性位点,具有更大的接触面积并缩短了离子传输距离。相比传统高温退火方法制备的同材料电极,具有纳米级结构的电极的锂离子电池的容量可以提高约 3 倍[46],且具有更好的倍率性和循环稳定性,如图 3(b)、(c)所示。虽然激光调控的纳米级结构有助于加速离子传输,但单一材料的电极仍无法同时满足高容量、高循环稳定性的要求,例如 SnO_2 阳极的锂离子电池虽然具有比较大的比容量,但循环性能较差;TiO_2 作为阳极材料循环稳定性好但容量较低[49]。激光加工由于具有高度定制化和适用性广的特点,也常被用于制备纳米级复合材料,大大简化了复合材料合成的复杂工艺。Fan 等[49]使用 PLD 技术交替地沉积了 SnO_2 和 TiO_2 薄膜来构建复合材料电极,如图 3(d)所示。电极中的 SnO_2 组分可以提供高的电池容量,但纯 SnO_2 电极会因为锂离子的插入而体积膨胀,产生较大的裂纹而无法保证电极完整性,如图 3(e)所示[50]。得益于 SnO_2/TiO_2 颗粒的紧密堆积,TiO_2 层可以有效地限制 SnO_2 的体积膨胀,从而显著提升循环稳定性,如图 3(f)所示。在提高电极电导率方面,Qin 等[51]通过激光沉积了 CoO-Co 纳米复合薄膜,如图 3(g)、(h)所示,其中 CoO 纳米晶体结构有助于提高容量和循环稳定性,如图 3(i)所示,而 Co 纳米粒子的复合有助于提高电子电导率并促进 Li_2O 的完全分解。

全固态电池由于安全性好和能量密度高,也受到了研究人员的广泛关注,而电极-电解质界面的构建和固态电解质薄膜的制备是固态电池研究的核心问题。常见的全固态电池通常会由于界面降解问题[52]而在正极和固态电解质之间存在较高的界面电阻[53],因此需要对界面进行改性处理。虽然可以通过涂覆 $Li_4Ti_5O_{12}$ 等氧化物的方式降低界面电阻,但会破坏离子和电子的有效传输路径。Sakuda 等[52]使用PLD技术将$80Li_2S\cdot 20P_2S_5$固态电解质

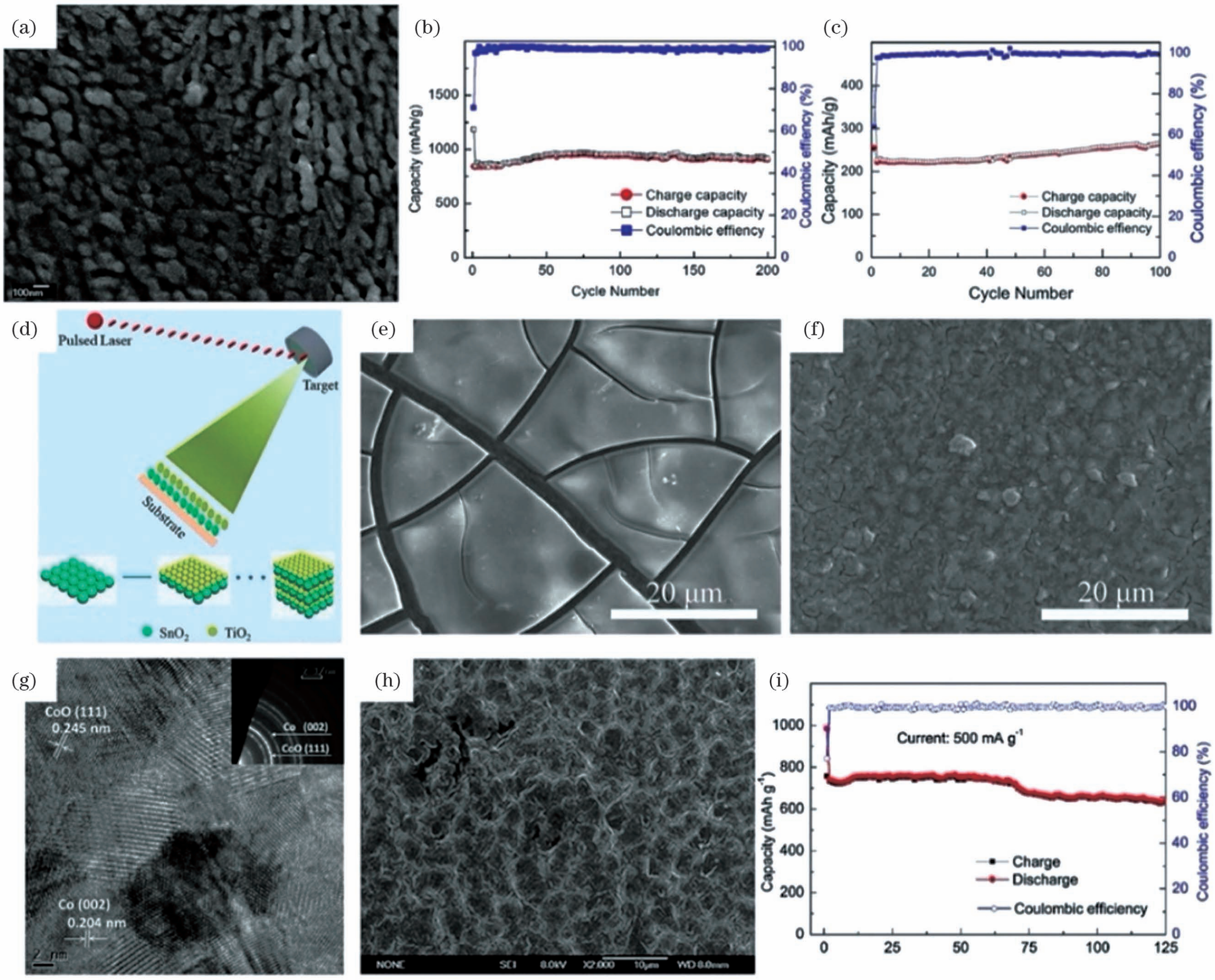

图 3　激光加工可充电电池电极。(a)PLD 制备的具有纳米级晶体结构的 Fe_2O_3 电极的 SEM 图像[46]；(b)具有纳米级晶体结构的锂离子电池的比容量和循环稳定性[46]；(c)没有纳米级晶体结构的锂离子电池的比容量和循环稳定性[46]；(d)脉冲激光交替沉积 SnO_2 和 TiO_2 复合薄膜的加工示意图[49]；(e)没有 TiO_2 复合层的锂离子电池在循环测试后的电极体积膨胀[50]；(f)具有 TiO_2 复合层的锂离子电池在循环测试后的电极体积膨胀[49]；(g) CoO-Co 复合电极的 TEM 图像[51]；(h) CoO-Co 复合电极的 SEM 图像[51]；(i) CoO-Co 复合电极的比容量和循环稳定性[51]

Fig. 3 Laser processing of rechargeable battery electrodes. (a) SEM image of Fe_2O_3 electrode with nanoscale structure prepared by PLD[46]; (b) specific capacity and cycling stability of lithium-ion batteries with nanoscale structure[46]; (c) specific capacity and cycling stability of lithium-ion batteries without nanoscale structure[46]; (d) schematic of the processing of pulsed laser deposited SnO_2 and TiO_2 composite film alternately[49]; (e) volume expansion of the electrode after cycling test for lithium-ion battery without TiO_2 composite layer[50]; (f) volume expansion of the electrode after cycling test for lithium-ion battery with TiO_2 composite layer[49]; (g) TEM image of the CoO-Co composite electrode[51]; (h) SEM image of the CoO-Co composite electrode[51]; (i) specific capacity and cycling stability of the CoO-Co composite electrode[51]

沉积在 $LiCoO_2$ 电极上，与传统界面改性方法相比，PLD 技术制备的固态电解质可以更加均匀且连续地包覆在电极表面；且与传统改性、无改性的电极相比，激光改性的电极具有更高的离子电导率、更好的循环稳定性和更高的电池容量，如图 4(a)所示。构建全固态电池的另一个挑战是固态电解质的制备。固态电解质薄膜通常需要高温加工，以获得更好的电化学性能，例如备受关注的石榴石固态电解质需要超过 1050 ℃ 的高温烧结，而高温处理严重限制了电极材料和界面工程的选择。Pfenninger 等[54]使用 PLD 技术在 330 ℃ 下实现了 $Li_7La_3Zr_2O_{12}$ 和 Li_3N 的多层复合材料的制备，如图4(b)所示。激

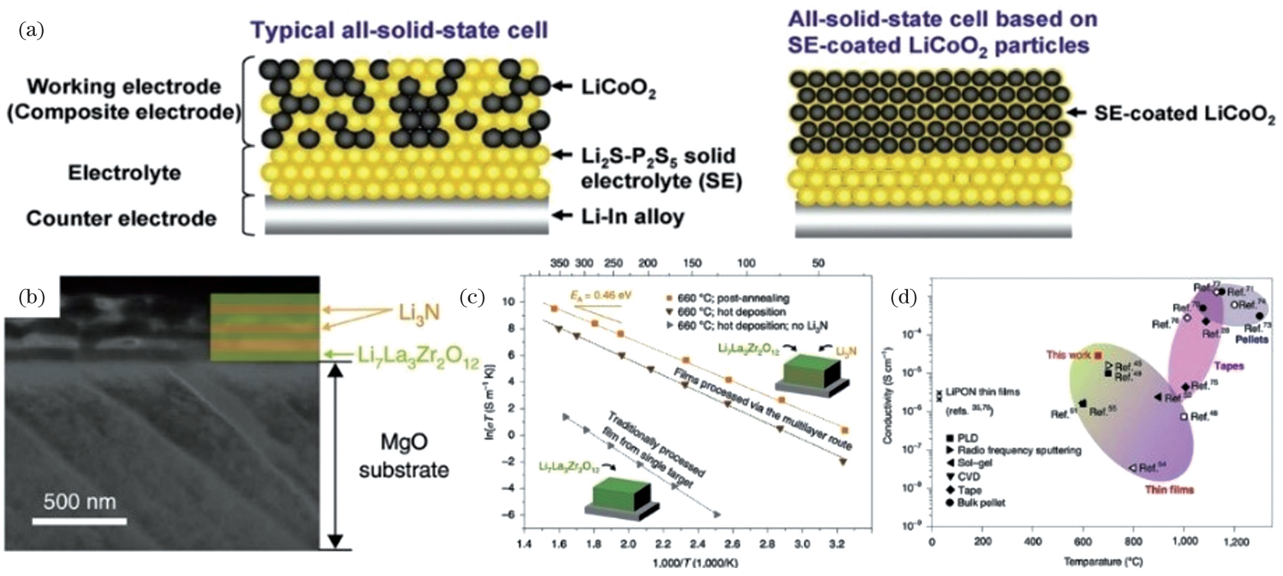

图 4　脉冲激光沉积加工全固态电池。(a)传统方法和 PLD 技术加工复合 $LiCoO_2$ 电极示意图[52]；(b)低温条件下，PLD 制备的多层复合材料电极的 SEM 图像[54]；(c)传统方法和 PLD 技术制备的电极薄膜在不同温度下的电导率[54]；(d)不同加工方法制备的电极薄膜的锂离子电导率[54]

Fig. 4　Pulsed laser deposition processing of all-solid-state batteries. (a) Schematic of processing composite $LiCoO_2$ electrode by conventional method and PLD method[52]; (b) SEM image of multilayer composite electrodes prepared by PLD under low temperature condition[52]; (c) conductivity of electrode films prepared by conventional method and PLD method at different temperatures[54]; (d) lithium ion conductivity of electrode films prepared by different processing methods[54]

光制备固态电解质不仅大幅降低了加工温度，而且得到的复合电解质薄膜具有更致密的结构、更高的电导率和离子迁移活化能，如图 4(c)、(d)所示。PLD 工艺具有很高的灵活性，可以实现多种材料、多种成分的薄膜沉积[55]。而 PLD 技术的主要缺点是复杂真空系统所导致的繁琐工艺和较低效率，这或许可以通过新颖的设备设计来克服，因此需要工程和物理方面的改进和优化[49]。

除了 PLD 工艺外，激光热解工艺和激光刻蚀工艺也在可充电电池制备领域有广泛应用。通过在 NH_3 氛围中[56]或聚酰胺酸溶液中[57]使用激光辐照电极材料，可以实现可控的 N 掺杂，如图 5(a)所示。与其他方法相比，激光热解的杂原子掺杂不仅更加便捷，而且得到的颗粒尺寸更小更均匀，如图 5(b)所示，具有更大的表面积和电化学性能，更有利于离子的快速转移和脱嵌；所制备的锂离子电池在电池容量、循环稳定性、高电流放电等方面也更有优势。除此之外，激光热解工艺还可以均匀可控地合成纳米颗粒。Kim 等[58]使用激光热解 GeH_4 来制备锗纳米颗粒，并且通过调节敏化剂气体流速，可以方便且精准地调控纳米颗粒的尺寸在 10～60 nm，如图 5(c)所示。将不同尺寸的锗纳米颗粒用作锂离子电池和钠离子电池的电极，结果表明，与商用的微米级颗粒制备的电极相比，激光热解得到的纳米级颗粒制备的电池具有更好的循环容量保持率和更快的充放电速率等，并且纳米颗粒尺寸越小，电池性能越优异，如图 5(d)所示。

虽然碳基材料在锂离子电池中具有广泛的应用，但锂合金体系的锂存储容量远高于碳基材料，而充放电过程中巨大的体积变化导致合金材料通常具有较差的循环稳定性和容量保持率，限制了其在锂离子电池领域的应用。而激光加工由于峰值功率高、热影响区小和空间分辨率高的特点，可以精准有效地调控材料的微结构来减缓体积变化，在这方面激光刻蚀工艺具有广泛的应用[59]。Sämann 等[60]将硅电极薄膜刻蚀为多孔结构，减小了离子嵌入过程中体积膨胀而导致的应力及活性物质断裂的风险，显著提高了循环稳定性，如图 5(e)所示。激光刻蚀工艺具有材料适用性广的特点，对传统加工方法难以加工的超硬材料[61]和透明介质材料[62]也能有效处理。在这方面，陈亮等[63]使用激光刻蚀工艺在石英表面构建了槽宽为 50 μm，深宽比达 5.4 的周期性微槽结构，如图 5(f)所示。而殷艺等[64]使用激光加工构建了尺寸仅为 2 μm的ITO电极，激光

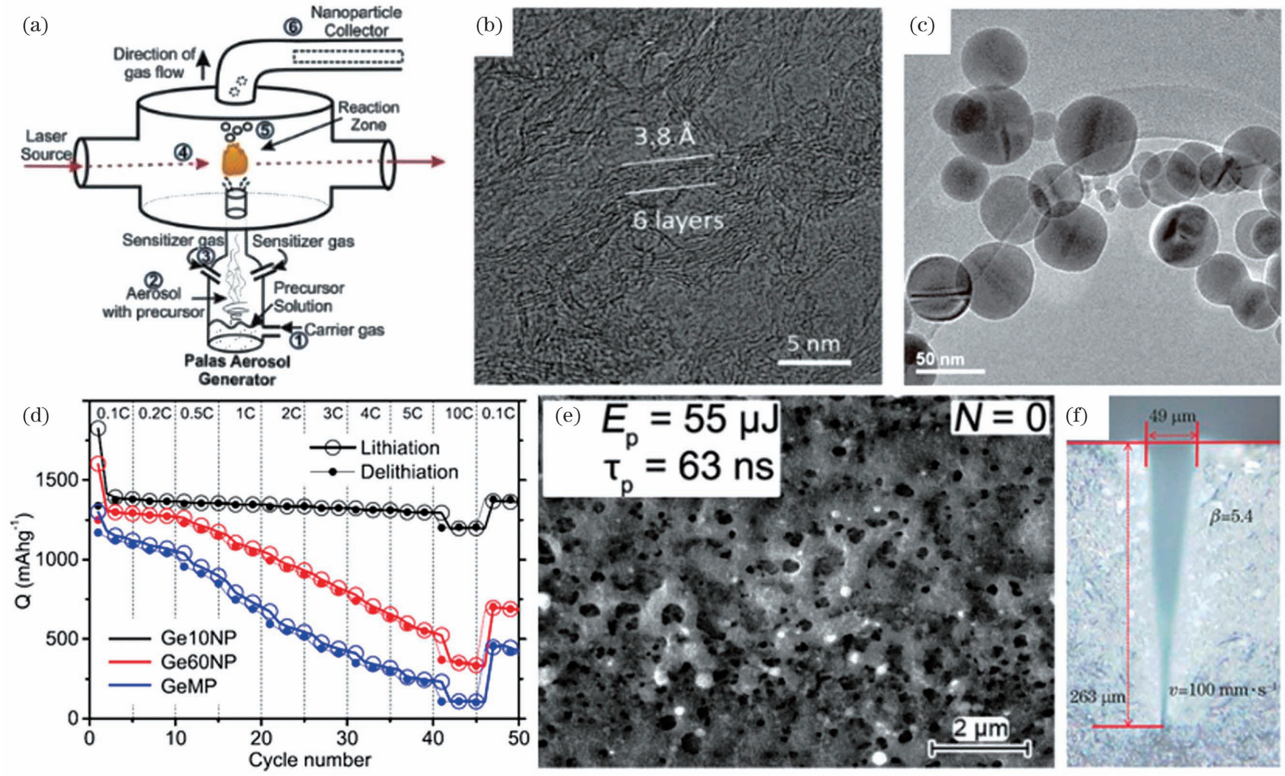

图 5 激光热解工艺和激光刻蚀工艺加工可充电电池电极。(a)使用激光热解工艺实现 N 掺杂的加工示意图[56];(b)激光热解工艺诱导 N 掺杂的石墨烯的 TEM 图像[57];(c)激光热解工艺制备直径为 60 nm 的锗纳米颗粒的 TEM 图像[58];(d)使用不同尺寸的锗纳米颗粒制备的可充电电池的循环容量保持率[58];(e)通过激光刻蚀技术制备的多孔硅电极的 SEM 图像[60];(f)激光刻蚀工艺制备的石英微孔的截面形貌[63]

Fig. 5 Laser pyrolysis process and laser etching process of rechargeable battery electrodes. (a) Processing schematic of N-doping by laser pyrolysis process[56]; (b) TEM image of N-doped graphene induced by laser pyrolysis process[57]; (c) TEM image of germanium nanoparticles with a diameter of 60 nm prepared by laser pyrolysis process[58]; (d) cycle capacity retention of rechargeable batteries prepared by germanium nanoparticles with different sizes[58]; (e) SEM image of porous silicon electrode prepared by laser etching technique[60]; (f) cross-sectional morphology of quartz micropores prepared by laser etching process[63]

加工精度远超传统方法,且能在表面刻蚀各种微结构并保持高导电率,在微纳能源器件领域具有重要的应用。

4 新型发电器件

4.1 激光加工太阳能电池

太阳能电池作为极具潜力的绿色可再生能源,一直以来都受到科学工作者的广泛关注。针对太阳能电池的研究工作主要集中在 2 个方面:光吸收材料和界面层材料[65-66]。PLD 技术不仅材料适用性广,而且成膜均匀、易于调控,因而在光吸收层沉积领域发挥着不可或缺的作用。而激光加工由于能量密度高和空间分辨率高的特点,在太阳能电池界面材料的调控方面有诸多应用。

在界面层材料调控方面,Park 等[67]使用 PLD 技术在 ITO 基底上制备了有纳米级取向性结构的 NiO 层,如图 6(a)所示,构建了 P-I-N 结构的太阳能电池。NiO 界面层可以有效地捕获空穴、阻止电子泄漏,从而提高载流子浓度和输出电压[68],最终实现了 17.3% 的能量转换效率。类似的,Sauvage 等[69]使用 PLD 技术制备了纳米级的 TiO_2 树状结构,如图 6(b)所示,不仅增强了光吸收能力,而且可以阻碍电子-空穴复合,将电子寿命提高了 1 个数量级,从而实现了更高的能量转换效率。除此之外,脉冲激光沉积的 Nb 掺杂的 TiO_2[70]、Nb_2O_5[71] 等界面层均可以起到阻止电子-空穴复合、降低界面电阻、提高能量转换效率的作用。除了 PLD 技术外,Haase 等[72]利用激光加工能量密度高的特点,使用脉冲激光在多晶硅表面的氧化硅层中选择性地刻蚀出多孔结构,如图6(c)所示,并实现了载流子

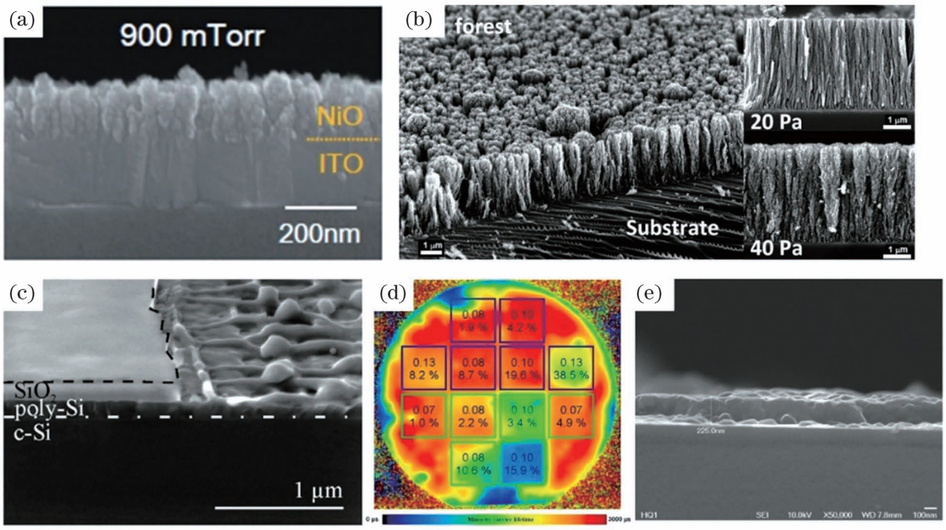

图 6　激光加工太阳能电池。(a)使用 PLD 工艺制备的取向性 NiO 纳米晶体结构的 SEM 图像[67]；(b) 使用 PLD 工艺制备的 TiO_2 树状结构界面层的 SEM 图像[69]；(c) 激光刻蚀的 SiO_2 界面层的 SEM 图像[72]；(d) 激光刻蚀的 SiO_2 界面层的载流子寿命[72]；(e) PLD 制备的 $CH_3NH_3PbI_3$ 光吸收层的 SEM 图像[73]

Fig. 6　Laser processing of solar cells. (a) SEM image of the oriented NiO nanocrystal structures prepared by the PLD process[67]; (b) SEM images of the interfacial layers of TiO_2 dendritic structures prepared by the PLD process[69]; (c) SEM image of laser etched SiO_2 interfacial layer[72]; (d) carrier lifetime of SiO_2 interfacial layer after laser etching[72]; (e) SEM image of $CH_3NH_3PbI_3$ photoabsorption layers prepared by PLD method[73]

寿命和能量转换效率的提高，如图 6(d)所示。

使用 PLD 技术制备太阳能电池光吸收材料的典型应用是 $CH_3NH_3PbI_3$ 光吸收层的沉积。相比其他薄膜制备技术，PLD 制备的薄膜晶粒更加均匀、密实，且易于调控薄膜的结构和带隙，如图 6(e)所示[73]，因而具有更高的能量转换效率。

PLD 技术不仅可以沉积多种材料的纳米级薄膜，而且能够精细控制所沉积薄膜的微观结构。影响沉积薄膜微观结构的 2 个关键因素是沉积环境和激光参数。多项研究表明，调整沉积的环境参数会改变沉积薄膜的形貌和密度。Ghosh 等[71]指出，PLD 在纯氩气环境中会沉积出致密无裂纹的 Nb_2O_5 薄膜，且随着沉积环境中氧含量的增加，薄膜逐渐形成更明显的柱状结构和裂纹，如图 7(a)所示。类似的，Park 等[67, 69]指出，随着沉积环境中氧分压的增加，密集堆积形态和平面形态变得更加多孔和粗糙。在合适的压力下(200 mTorr，1 Torr=133.322 Pa)，会沉积出有序的圆柱状纳米结构，而当氧气含量过高时(大于 500 mTorr)，表面显得相对粗糙且包含空隙，形成树状多孔结构，并且随着氧气压力的进一步升高，结晶度和首选取向度会降低，最终形成松散堆积和无序的微观结构，如图 7(b)所示。除此之外，激光沉积参数也是影响薄膜结构的关键因素。随着脉冲激光沉积时间和功率的增加，薄膜厚度、致密度、光吸收特性及电池容量等都会受到显著影响[71]。

4.2　水汽自发发电材料和器件

水汽自发发电是一种利用水与先进功能材料相互作用直接产生电能的绿色能源技术[74]。石墨烯材料由于优异的物理化学性质、巨大的比表面积、与水分子独特的相互作用而被认为是水汽自发发电器件的理想载体[75-78]。而激光加工技术可以选择性地辐照 GO 的特定区域以去除其表面的官能团，激光辐照的区域会被还原为 rGO，优异的导电性使得石墨烯材料可以用作发电器件中的电极和导线[79]；未被激光辐照的区域仍保持为 GO，可调节的电化学性质使得石墨烯材料常被用作水汽自发发电器件的功能材料[80]。

Cheng 等[80]利用 DLW 技术在 GO 薄膜上原位还原出 rGO 叉指电极，如图 8(a)所示，并利用湿气辅助的电化学极化技术在叉指电极间的 GO 区域构建梯度化的含氧官能团分布，从而实现了水汽自发发电器件在 GO 薄膜上的原位制备。当器件置于高湿度环境中时，单个水汽自发发电器件可以产生 60 mV 的开路电压和 12 mA·cm^{-2} 的比面积电流输出。采用 DLW 技术在 GO 薄膜上进行原位加工，所得到的水汽自发发电器件具有很好的柔韧性，并且能够使用可编程激光进行高密度集成。

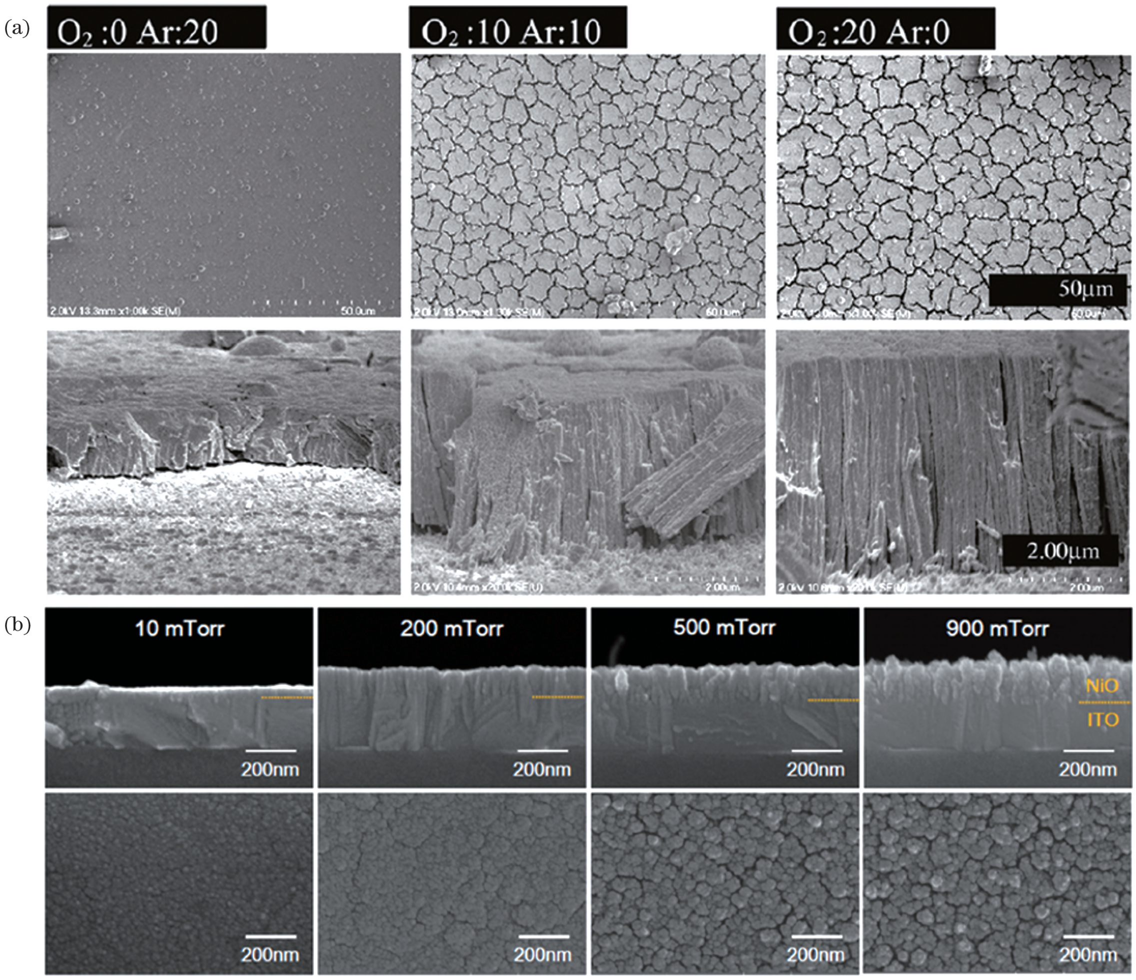

图 7 不同环境参数下使用 PLD 工艺沉积薄膜的形貌。(a)不同气氛环境下 PLD 工艺沉积的 Nb_2O_5 薄膜的形貌[71]；(b)不同氧气压力下 PLD 工艺沉积的薄膜的形貌[67]

Fig. 7 Morphology of films deposited by PLD process under different environmental parameters. (a) Morphology of Nb_2O_5 films deposited by PLD process under different atmospheres[71]; (b) morphology of films deposited by PLD process under different oxygen pressure[67]

Lee 等[81]通过对激光焦点位置的调节，利用不同聚焦程度下局部热效应的差异，实现了水汽自发发电器件的一步化激光直写制备，无需额外的电化学极化处理，如图 8(b)所示。所制备的水汽自发发电器件可以产生 0.23 V 的开路电压和 0.4 $\mu A\cdot cm^{-2}$ 的比面积电流输出，如图 8(c)所示，能够利用人呼吸过程的湿度变化产生电能，为发光二极管供电。除此之外，由于材料适用性广的特点，激光加工可以将碳纳米管等多种碳材料一步化地制备为任意尺寸和形状的水汽自发发电器件。为了解决水汽自发发电器件输出功率低的问题，Huang 等[82]使用激光辐照的局部热效应梯度化地还原了 GO 三维组装体，如图 8(d)所示，并在 GO/rGO 电极处分别构建了肖特基接触和欧姆接触。通过激光辐照一步化制备的单个水汽自发发电器件在高湿度环境中可以产生 1.5 V 的电压输出，如图 8(e)所示，通过简单的集成即可产生 18 V 的输出电压，足以为发光二极管、显示屏等商用器件供电。Liang 等[83]则利用激光加工精度高、热影响区小的特点，通过可编程激光将 GO 纤维分段的原位还原为 rGO 段/GO 段，如图 8(f)所示。间隔分布的 rGO 可以作为水汽自发发电器件的电极，通过电化学极化处理的辅助，完成了单根 GO 纤维上水汽自发发电器件的高密度集成，使单根纤维的输出电压达到 1.3 V。激光的原位加工还使得水汽自发发电器件具有很好的柔韧性，可以轻松集成到纺织品中用作自供电的可穿戴设备，如图 8(g)、(h)所示。

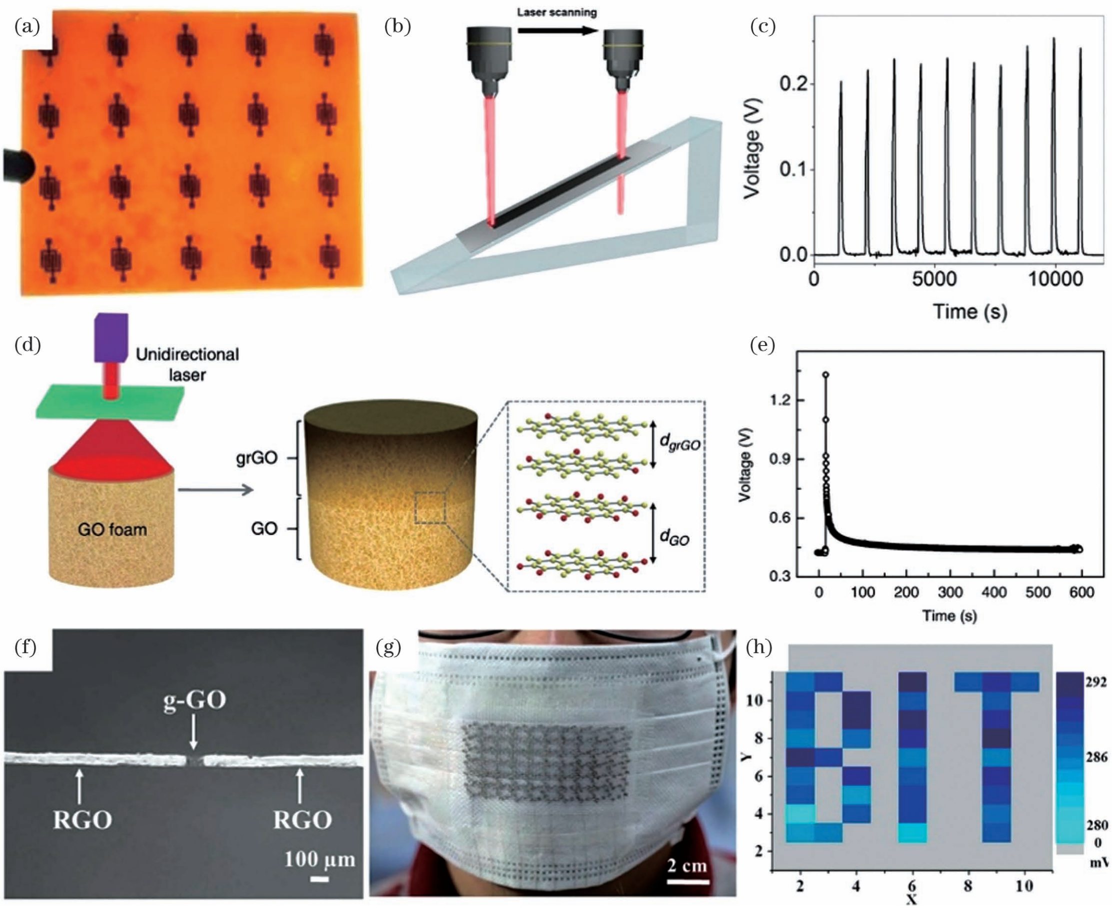

图8　激光加工水汽自发发电器件。(a)利用DLW技术在GO薄膜上原位还原出叉指电极的光学照片[80]；(b)(c)激光构建GO含氧官能团梯度分布的加工示意图及所构建的水汽自发发电器件的产电性能[81]；(d)(e)利用激光局部热效应梯度化还原GO三维组装体的加工示意图及所构建的水汽自发发电器件的产电性能[82]；(f)激光在GO纤维上原位构建出水汽自发发电器件的SEM图片[83]；(g)(h)水汽自发发电器件在纺织品中的集成和产电性能[83]

Fig. 8　Laser processing of water-enabled electric generators. (a) Optical photograph of interdigital electrodes fabricated *in situ* on GO films using DLW method[80]; (b)(c) processing schematic of the gradient distribution of laser-constructed GO oxygen-containing functional groups and the power generation performance of constructed water-enabled electric generators[81]; (d)(e) processing schematic of the reduced GO 3D assemblies using laser local thermal effect and the power generation performance of constructed water-enabled electric generators[82]; (f) SEM image of water-enabled electric generators constructed *in situ* on GO fibers using laser processing[83]; (g)(h) integration of water-enabled electric generators in textiles and electrical generation performance[83]

5　激光加工柔性能源器件

电子器件向着智能化、高度集成化和可穿戴化发展的同时，也对新型能量转化和存储器件提出了更高的要求。较差的力学性能、单一的结构严重限制了传统的能源器件在可变形的柔性环境中的应用[84-85]。而DLW技术作为一种无需掩模的一步化加工方法，由于空间分辨率高、定制化程度高、材料适用性广的特点，常被用于在多种基底上原位制备柔性的功能器件[86]。

Liu等[87]利用DLW技术在ITO基底上选择性地沉积了超薄的Ni电极(宽度小于5 μm)，在保持3×10^4 S·cm^{-1}电导率的同时，还具有84%的光学透明度和出色的柔韧性。随后通过在Ni电极上沉积MnO_2纳米片和导电纳米纤维，完成了透明、柔性的全固态超级电容器的制备。超级电容器整体具有大于80%的透射率、80.7 mF·cm^{-2}的能量密度及优异的循环稳定性。超级电容器在高度卷曲、折叠、褶皱的情况下均未表现出明显的性能下降，在各种变形状态下均能为30个发光二极管供电，显著拓展了超级电容器在柔性、透明场景下的应用空间，如图9(a)所示。类似的，Zang等[88]使用

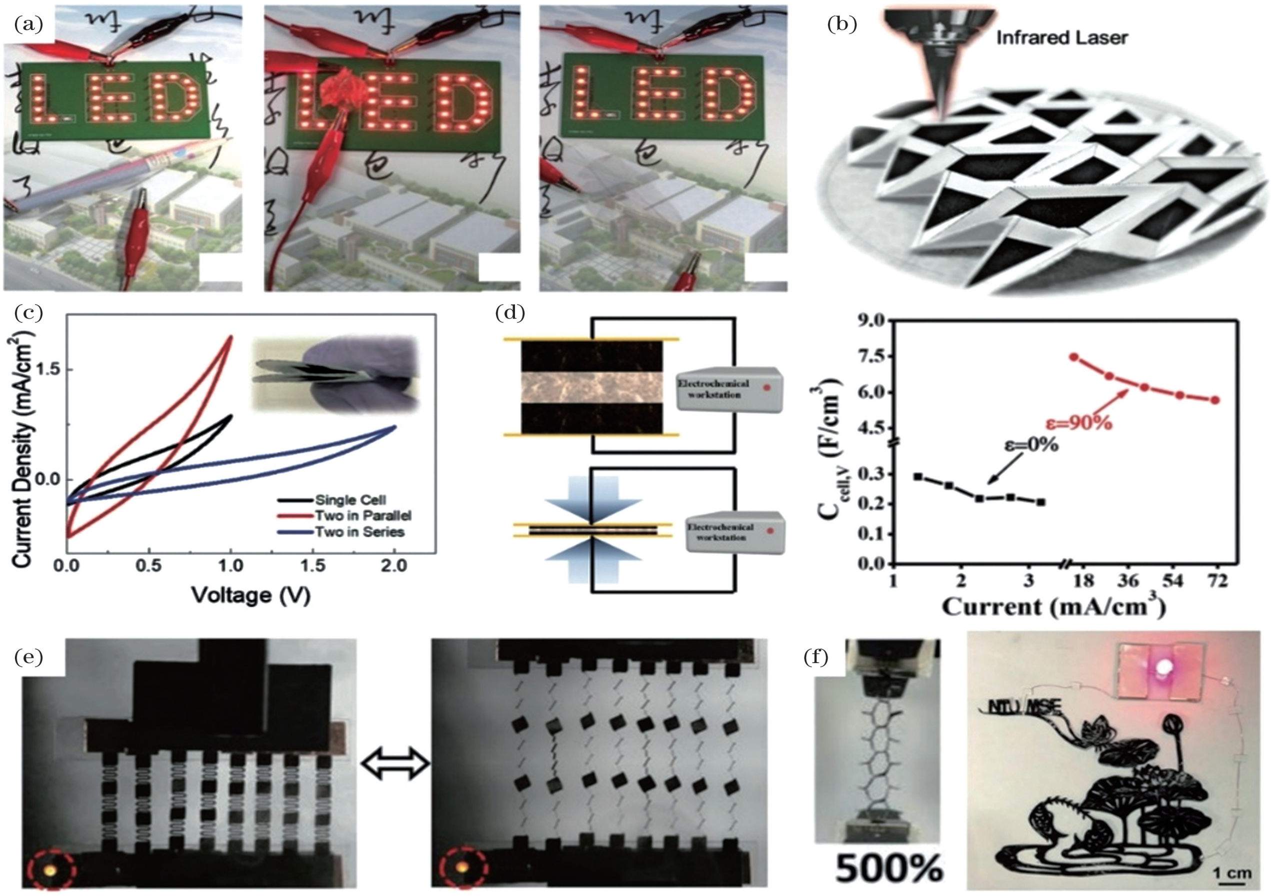

图 9 激光加工柔性能源器件。(a)激光加工的柔性透明电容器在卷曲、褶皱、折叠变形下为 LED 灯泡供电[87];(b)(c)激光原位还原制备折纸型能源器件及其在不同折叠状态下的输出功率[88];(d)激光加工制备的可压缩电容器及其在不同压缩状态下的能量密度[89];(e)激光直写加工的蛇形岛桥结构的水汽自发发电器件在不同变形状态下为发光二极管供电[91];(f)激光加工可延展剪纸结构的超级电容器[92]

Fig. 9 Laser processing of flexible energy devices. (a) Laser-prepared flexible transparent capacitor for powering LED bulbs under curling, creasing, and folding deformation[87]; (b)(c) laser *in situ* preparation of origami-type energy devices and their output power in different folding states[88]; (d) compressible capacitors prepared by laser processing and their energy density at different compression states[89]; (e) water-enabled electric generators prepared by DLW to power light emitting diodes in different deformation states[91]; (f) laser processing of supercapacitors with stretchable paper-cut structure[92]

DLW 技术,在浸有导电油墨的纸质基底上原位还原出碳化钼-石墨烯多孔电极,如图 9(b)所示。碳化钼-石墨烯电极不仅具有 30 Ω 的方阻值,而且 DLW 加工可以将电极原位嵌入到纸质基底中,在 750 次弯曲折叠后仍保持电导率衰减幅度小于 5%。然后 Zang 等[88]将压电材料和固态电解质与碳化钼-石墨烯电极集成,并设计为折纸结构的能源器件,不仅可以通过简单的纸张折叠和组装就能实现器件的串并联和高度可延展性,而且可以显著降低器件尺寸、提高能量密度,如图 9(c)所示。7 个压电发电机通过折纸结构并联后可以达到电压为 150 V 和电流为 80 μA 的输出,超级电容器则可以达到 14 mF·cm^{-2}的能量密度,并且通过折纸结构的组装可以进一步提高能量密度或改变串并联的方式。而在输出功率调节方面,Shao 等[89]则通过柔性电容器的拉伸和压缩满足输出功率和能量密度的条件。以三聚氰胺泡沫为骨架,制备了柔性可压缩的 GO 三维组装体,并通过 DLW 技术在上下表面原位还原出 rGO 电极,从而实现具有很好柔韧性和可延展性的超级电容器的制备。电容器在高度压缩和拉伸状态下均具有高稳定性,且可以实现 0.04～1 mWh·cm^{-3}能量密度的可控调节,如图 9(d)所示。

现有的先进功能材料通常具有很好的可弯曲

性，但材料本身的可延展性通常很差[90]。受益于 DLW 加工的高度可定制化，Yang 等[91]使用 DLW 技术在柔性 GO 薄膜上原位还原出具有蛇形岛桥结构的水汽自发发电器件和互联电路。蛇形岛桥结构可以将器件的面内拉伸变形转换为蛇形互联导线的面外屈曲变形，从而保证发电器件（岛结构）不会发生破坏。该水汽自发发电器件可以在高度弯曲、100%拉伸状态下保持稳定的输出功率，均能为发光二极管供电，如图 9(e)所示。类似的，Lü 等[92]利用可编程激光将全固态超级电容器设计为多种剪纸结构，将拉伸应变转换为弯曲应变，从而避免器件的破坏，并在 500%的拉伸变形下能保持性能稳定，如图 9(f)所示。

6 结束语

综述了激光微纳加工技术在新型能源器件领域应用的研究进展。在超级电容器方面，激光加工可以高定制化地制备电容器电极并对材料进行改性，以适应微型化、集成化、高能量密度的发展需求；在可充电电池方面，脉冲激光沉积技术不仅能够制备高质量的电极、电解质，而且可以对微观结构进行精准调控、优化接触界面，从而实现更高的功率密度、更好的循环稳定性和更快的充放电速率；在新型发电技术方面，激光微纳加工由于高度定制化、空间分辨率高的特点，在器件的微观结构设计、功能材料改性、器件性能优化等方面有诸多应用。尽管激光微纳加工在新型能源器件领域已经取得了极其可观的进展，但仍有许多问题有待解决与探索。例如，激光诱导材料微结构调节主要基于它们的相互作用，而激光作用机理仍在发展，对其认识和理解仍不够完善，在很大程度上阻碍了以合理设计的方式对材料进行调控。其次，激光加工很难控制空间厚度或结构缺陷的形式，需要进一步深入了解激光加工的优势和精准控制策略，以实现材料或者器件的更精确调控。最后，目前激光加工的研究主要集中在前驱体材料或表面结构的调控上，在更复杂的场景下的应用还有待进一步探索。随着对激光作用机理的深入理解和激光精确控制的进一步发展，结合材料、化学、物理、机械等多学科的交叉研究，激光微纳加工在新型能源器件领域的应用定会取得新的突破。

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Research Advancement on Laser Micro-Nano Processing of New Energy Devices

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Abstract

Significance Due to the increasing energy crisis and environmental pollution problems, new energy technologies have been a research hotspot among scientists. Although several energy devices, such as supercapacitors, lithium-ion batteries, solar cells, new energy storage, and power generation devices, having been developed, low energy density, complex preparation process, monotonous structure, and poor mechanical properties have severely limited their application in practical scenarios. Traditional processing methods suffer from complex processes, difficulty in processing microdevices, and the inability to precisely regulate material properties, making it difficult to process high-performance energy devices. With high peak energy density, small heat-affected zone, wide material applicability, high spatial resolution, and customizability, laser processing is often used to increase the energy density of energy devices and integrate microdevices. Thus, it has great research value and application potential in the field of precision processing of advanced materials and devices.

Progress The ultra-high peak power density of the laser can produce strong interactions with the material in a localized area of action, which can finely modulate the microstructure of the electrode surface and significantly increase the energy density of the double-layer capacitor (Fig. 1). For pseudocapacitor supercapacitors, laser treatment can significantly improve the energy storage capacity by doping active materials or heteroatoms into the electrode material or enhance the kinetics of redox reactions and improve cycling stability through the surface morphology modulation (Fig. 2).

Lithium-ion batteries play a significant role in life and production. However, the slow reaction kinetic process limits the output power of lithium-ion batteries. The expansion of electrodes during charging and discharging affects the life and safety of lithium batteries. The pulsed laser deposition technology can finely regulate the microstructure of electrodes and develop composite materials, which is conducive to improving the working area of electrodes, reducing the ion transport distance, and increasing the electrical conductivity of electrons and ions; thereby, significantly increasing the energy density and output power of lithium-ion batteries (Fig. 3). Additionally, pulsed laser deposition technology can prepare ultra-thin, dense, and uniform films, which can significantly reduce interface resistance to ensure high ion conductivity and high output power (Fig. 4). Besides, the use of laser etching technology can conveniently control the microstructure of electrode materials or selectively construct composite materials. It can also alleviate the problems of poor cycle stability and low capacity retention caused by volume changes during charging and discharging (Fig. 5).

Laser processing also has important applications in constructing light-absorbing and interfacial layer materials for solar cells. Nanoscale-oriented structures can be prepared on the electrode surface using pulsed laser deposition techniques, which can prevent electron-hole complexation, reduce interfacial resistance, and improve the energy conversion efficiency (Fig. 6). Functional light-absorbing for solar cells can also be prepared using pulsed laser deposition technology. Compared with traditional methods, the grain size of the photoabsorption layer prepared using pulsed laser deposition technology is more uniform and dense. It can easily regulate the structure and band gap of the film, and the microstructure can easily be adjusted to achieve higher light-absorption efficiency (Fig. 7).

Due to the local interaction between the laser and graphene oxide, the direct laser writing technique is often used to prepare water-enabled electric generators. Direct laser writing technology can reduce irradiated graphene oxide regions to conductive reduced graphene oxide to serve as electrodes and interconnecting circuits. Thus, enabling easy *in situ* construction and integration of water-enabled electric generators on graphene oxide assemblies is realized. However, the thermal effect of laser processing can partially reduce the graphene oxide material. Thus, three-dimensional water-enabled electric generators can be prepared in a controlled manner to obtain higher output power (Fig. 8).

Laser processing has the characteristics of high spatial resolution and strong customization. It can be used to prepare electrode materials with high light transmittance and good flexibility. Simultaneously, the device can be designed into a specific structure to obtain ductility; thus, it has important applications in the field of flexible electronics (Fig. 9).

Conclusions and Prospects　Laser processing has obvious advantages and potential in the field of high-performance energy devices. Currently, pulsed laser deposition technology, direct laser writing technology, laser induction technology, and laser etching technology have achieved many successful applications in material modification, device functionalization and miniaturization, electrode preparation, and structural modulation. Supercapacitors, lithium-ion batteries, new energy devices, and flexible electronics prepared using laser processing have significant advantages in terms of energy density, stability, and energy conversion efficiency miniaturization and integration. Although laser processing has made considerable progress in the field of energy devices, there are still many issues to be addressed. For example, the knowledge and understanding of the mechanism of laser-material interaction are still imperfect. It is also difficult to control the spatial thickness or form of structural defects using laser processing. Additionally, the current research on laser processing mainly focused on regulating precursor materials; its application in more complex scenarios needs to be further investigated. With a deeper understanding of laser action mechanisms and further development of laser precision control, it is expected that the applications of laser processing in the field of new energy devices will make breakthroughs.

Key words　laser technique; energy device; micro-nano processing; energy conversion and storage; advanced material

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