

飞秒激光调控钙钛矿量子点玻璃的析晶和光学性能研究进展

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摘 要: 全无机钙钛矿(CsPbX₃, X = Cl, Br, I)量子点玻璃因其强光吸收系数、高荧光量子效率、可调的能带宽度和较高的载流子迁移效率等优异的光学性能, 受到研究者的广泛关注。超短脉冲激光即飞秒激光加工透明材料已被证明是构建三维光子器件结构的有效方法, 在非线性光学、光学数据存储和纳米光子学等领域有着广泛的应用。本文根据飞秒激光与钙钛矿量子点玻璃相互作用, 综合介绍了飞秒激光调控钙钛矿量子点玻璃的析晶和光学性能研究进展, 并为飞秒激光作用钙钛矿量子点玻璃的未来的研究和应用提供了新的思路和见解。

关键词: 钙钛矿量子点; 玻璃; 飞秒激光

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全无机钙钛矿量子点(CsPbX₃, X=Cl, Br, I)凭借其优异的光学与电学性能, 如高量子产率(QY)、高纯度、可调谐发光波长、高缺陷容忍度和高载流子扩散速率等^[1-5], 在太阳能电池^[6-7]、发光二极管(LED)^[8-9]、光电探测器^[10-12]和激光^[13-14]等光电领域具有广阔的应用前景。然而, 钙钛矿量子点由于其离子结构和较大的表面能, 容易受到氧气、水分、高温和强光环境的侵蚀而分解^[15-16]。为了提高其稳定性并保持较高的发光效率, 研究人员开始将这些 CsPbX₃ 量子点掺杂到具有良好热稳定性、机械稳定性和化学稳定性的高透明玻璃基质中^[17-19]。近年来, 许多研究者们已经成功在硅酸盐^[20-30]、锗酸盐^[31-33]、碲酸盐^[34-37]、磷酸盐^[38-42]和硼酸盐^[43-44]等玻璃体系中成功析出钙钛矿量子点, 并广泛应用在光学探测^[37, 45-46]、X射线成像^[47-48]、激光^[49]、光学信息存储^[50]和光学防伪^[51]等领域。

钙钛矿量子点玻璃最常用的制备方法是熔融淬火法。将钙钛矿量子点的组成元素的化合物和玻璃成分的氧化物进行混合研磨, 放置于刚玉坩埚高温熔融一段时间, 随后急速冷却, 以得到钙钛矿量子

点前驱体玻璃。随后通过热处理过程, 可在玻璃基质中析出钙钛矿量子点^[52]。基于玻璃的传统析晶理论, 通过热处理使玻璃温度升高至玻璃化转变温度, 从而降低玻璃的黏度, 促使原子迁移并重新分布, 最终形成晶体结构。这种热处理诱导方法能够使玻璃整体均匀地析出 CsPbX₃ 量子点, 并且通过调节热处理温度和时间, 可实现对玻璃析晶状态及量子点结晶尺寸的调控, 进而调节量子点的发射波长。尽管这种利用热场诱导钙钛矿量子点析出的方法较为简便, 但其尺寸分布受限于玻璃的均匀性, 表现出无序分布的特征。除此之外, Xiang 等^[53]还发现利用应力诱导钙钛矿量子点在玻璃表面析出现象。与传统的热诱导相变机制不同, 玻璃网络的断裂为量子点成核和生长提供了能量, 降低了成核和晶体生长的能量势垒, 使量子点更容易在玻璃表面析出。Zhang 等^[43]基于此设计制备了 Pb²⁺响应的机械应力响应玻璃, 将含有 Cs、Br、Eu 的硼酸盐玻璃与含铅材料混合研磨, 利用 CsPbBr₃ 的 Pb²⁺浓度依赖性绿色发射作为指示信号, Eu³⁺的独立红色发射作为参考信号, 实现了 Pb²⁺的传感。不同玻璃体系抗水的腐蚀能力不同, 磷酸盐玻璃在潮湿环境下

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容易潮解, 玻璃网络结构会受到水分子的侵蚀而断键。因此 Li 等^[41]发现可以利用水诱导出 CsPbBr₃ 量子点玻璃析晶, 并随着侵蚀时间增长, 发光强度逐渐增强。Wang 等^[42]利用水降低玻璃的非均匀成核势垒来诱导结晶, 成功制备出了全可见发光的 CsPbX₃ 钙钛矿量子点玻璃, 并且实现了图案化防伪功能。

然而无论是热处理方法无法定位析晶, 还是应力、水诱导析晶带来的表面重金属 Pb 的毒性, 都极大的限制了其应用前景。超短脉冲激光即飞秒激光加工透明材料已被证明是构建三维光子器件结构的

有效方法, 在非线性光学、光学数据存储和纳米光子学等领域有着广泛的应用^[54–57]。飞秒激光通过多光子吸收与透明材料相互作用, 无需考虑材料的吸收或引入新的吸收中心, 并且聚焦后的超短脉冲激光能量高度局域^[58–60]。这种处理的高空间分辨率是由连续非线性光学过程引起的激光焦点处原子的快速重新分布实现的^[61]。该技术已成功地应用于引入微裂纹、改变微区折射率和形成纳米晶体^[62–63]。如表 1 所示, 相对于传统的钙钛矿量子点的制备方法, 飞秒激光更适用于在透明玻璃材料内部析出钙钛矿量子点。

表 1 不同方法制备钙钛矿量子点玻璃的优缺点

Table 1 Advantages and disadvantages of different preparation methods of perovskite quantum dots (PQDs) embedded glass

Preparation method	Advantage	Disadvantage
Thermal treatment	Simple preparation and adjustable crystal size	Unlocatable crystallization
Mechanical treatment	Stress sensing, ion exchange	Damaged structure, poor stability
hydration treatment	Humidity sensing	Damaged structure, poor stability
Femtosecond laser irradiation	Adjustable crystal size, localization crystallization and low toxicity	High requirements on equipment

当前, 飞秒激光作用钙钛矿量子点玻璃的研究已经取得了重要的研究进展, 这些研究扩展了钙钛矿量子点玻璃的潜在应用领域。本文重点综述了飞秒激光调控钙钛矿量子点玻璃的析晶行为和光学性能的最新研究进展。同时, 展望了未来飞秒激光在钙钛矿量子点玻璃方面的发展趋势, 以便为钙钛矿量子点玻璃的应用和研发提供新的思路 and 方向。

1 飞秒激光调控钙钛矿量子点玻璃的

析晶研究进展

飞秒激光由于其超短的脉冲宽度, 有着超高的峰值功率, 因此飞秒激光可以通过非线性多光子吸收与玻璃之间产生有效的相互作用。一般来说, 飞秒激光作用形成微晶玻璃是通过高重复频率的飞秒激光, 即 2 个相邻激光脉冲的时间足够短, 从而达到积累热量的效果, 使得提升至足够的温度使玻璃析晶^[64–65]。低重复频率的飞秒激光却可以凭借高的峰值功率作用玻璃中产生大量光电子并在几个皮秒内将动能转移到晶格振动中, 从而将晶格的温度瞬间提高到几千摄氏度^[66]。这种高峰值功率的飞秒激光会破坏玻璃网络结构, 有利于原子迁移和重排, 结合低温热处理仍可实现析晶。

1.1 调控析晶尺寸

2019 年, Huang 等^[50]首次利用飞秒激光与热处

理方法相结合, 成功在硼硅酸盐钙钛矿量子点前驱体玻璃中三维空间选择性析出明亮的 CsPbBr₃ 量子点。如图 1a 所示, 聚焦后的 1 kHz 的 800 nm 飞秒激光作用于钙钛矿前驱体玻璃, 使得玻璃内部出现裂纹, 被辐照的区域形成了棕色的圆斑。在电子显微镜下发现这是激光能量高度局域诱导形成的钙钛矿晶核, 并随着低温热处理进一步长大形成钙钛矿量子点。未被飞秒激光辐照的玻璃区域并没有钙钛矿量子点的形成。通过控制飞秒激光的功率密度, 可以实现发光强度和波长的调控。而在相同飞秒激光的脉冲能量的作用下, 较长的作用时间可以增大 CsPbBr₃ 晶核数量。由于激光作用区域的 CsPbBr₃ 元素数量一定, 在后续热处理长大的量子点尺寸更小, 因此可以通过控制飞秒激光的脉冲能量和作用时间来控制量子点的尺寸。随后 Jin 等^[67]在研究了 ZnO 对玻璃析晶性能的影响后, 也系统了探究飞秒激光参数作用下对钙钛矿量子点玻璃三维光学信息存储的应用。Du 等^[68]制备了低熔点的硼磷酸盐玻璃, 并探究了飞秒激光波长、脉冲频率和峰值功率对钙钛矿量子点玻璃析晶性能的影响。Hu 等^[69]同样利用飞秒激光结合热处理在空间中选择性析出了 CsPbBr₃ 量子点。随着飞秒扫描速率的降低和脉冲能量或重复频率的增加, 发射逐渐由蓝色转变为青色和绿色, 也表明可以通过飞秒激光实现 CsPbBr₃ 量子点尺寸的调谐(见图 1b~图 1c)。Sun 等^[70]利用飞秒激光诱导的超快热效应, 在玻璃中直接刻写

CsPbI_3 , 表现出高效的深红色光致发光, 内部量子效率为 23%。通过改变飞秒激光的重复频率, 也可

通过改变析出 CsPbI_3 量子点的大小, 得到可控发射波长的红光(见图 1d~图 1e)。

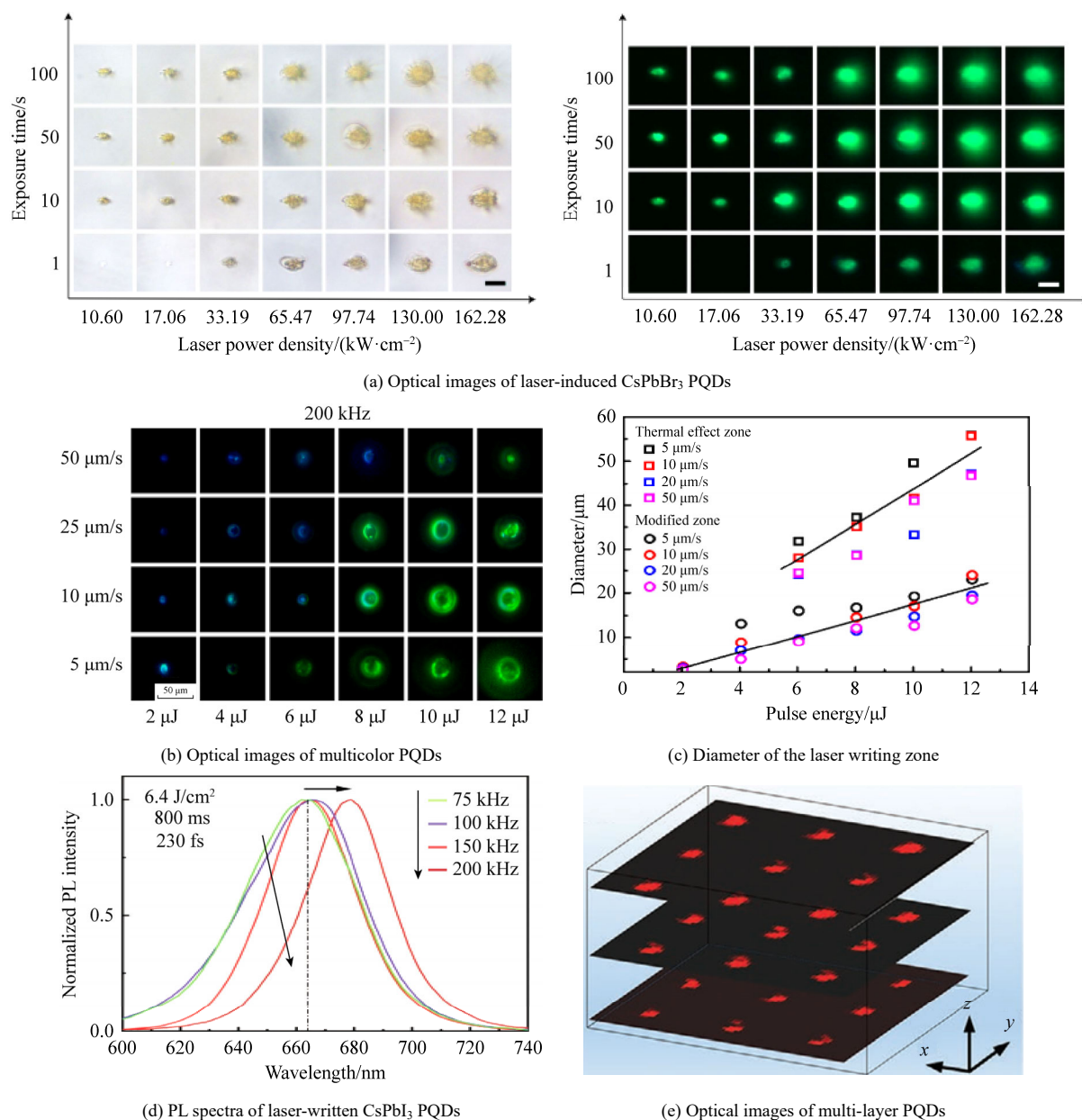


图 1 飞秒激光调控钙钛矿量子点玻璃的析晶尺寸^[50, 69-70]

Fig. 1 Femtosecond laser controls the crystallization size of PQDs embedded glass^[50, 69-70]

1.2 调控析晶类型

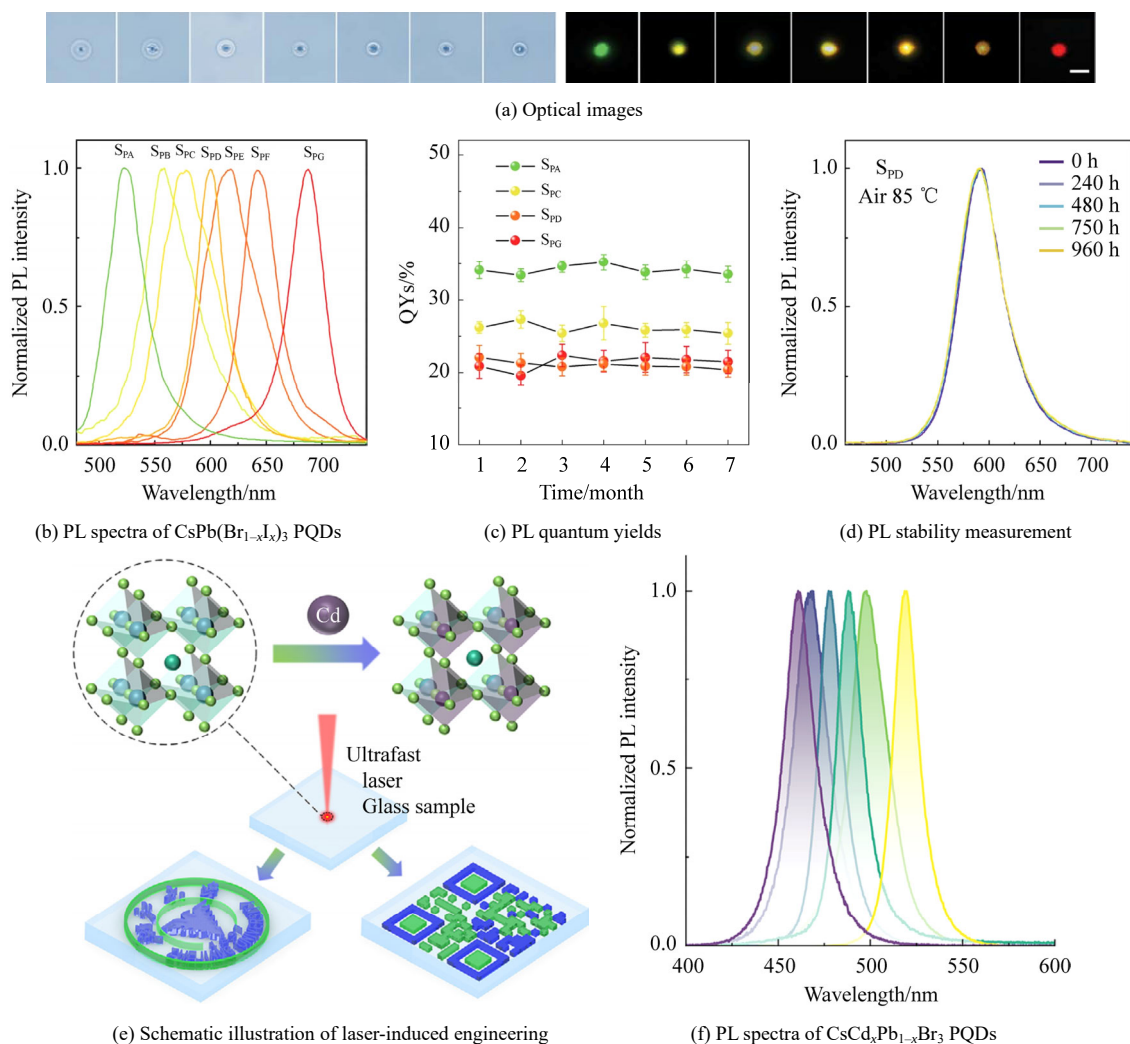
混合卤素钙钛矿量子点在黑暗环境下稳定, 而在强光照射下易产生分解或卤素偏析引起发射峰位极大变化^[8, 71]。在热力学理论中, 这是由于光照产生的载流子聚集到不同卤化物相中比母相更低带隙的成核相, 从而导致形成了新的带隙的混合卤素钙钛矿量子点^[72-73]。钙钛矿量子点玻璃具有出色的物化稳定性, 即使在热场环境中也不会发生混合卤素胶体量子点的卤素偏析或者阴离子交换反应^[15]。因

此按照传统热处理方法制备的钙钛矿量子点玻璃, 其晶体的类型与前驱体玻璃组分的卤素含量、比例有关, 而热处理温度变化只能通过改变晶体尺寸略微的调节其发射峰位移动, 而且单一的热处理温度只能得到单一发射的钙钛矿量子点^[24]。在玻璃中实现可控的混合卤素宽带可调谐发射的钙钛矿量子点在构建三维光子器件及光学信息存储领域具有重大意义。

2022 年, Sun 等^[74]研究了一种新的策略来设计

玻璃内部纳米晶的局部化学性质。利用飞秒激光在超短时间内注入能量，造成强烈的热积累效应，从而提高玻璃体系液相线以上的局部压力和温度，诱导局部液相纳米相分离，从而实现了玻璃内部成分可调的钙钛矿量子点的三维直接光刻。他们使用典型的含有铯、铅和卤化物的硼磷酸盐玻璃作为光刻基质，利用铯、铅和卤化物离子的高迁移率促进了钙钛矿纳米相与玻璃基体的分离以及随后组成可调谐的钙钛矿量子点。通过优化飞秒激光脉冲持续时间和重复时间，实现了所需的超快激光直接光刻工艺技术，制备了宽带可调发射颜色的钙钛矿量子点玻璃(见图 2a)，对应于图 2b 中 520~690 nm 的宽带可调谐发射。此外，他们还成功的制备了 Cl-Br-I

共掺杂的钙钛矿量子点玻璃，实现了 480~700 nm 的全彩三维信息存储。并且制备的量子点在高功率紫外线、有机溶液或高温环境中均有较为出色的稳定性(见图 2c~图 2d)。结合商用紫外或者蓝色 LED 阵列，这个技术还可以应用于制造 u-LED、高分辨率显示器和三维全息显示器件。随后于 2023 年 Sun 等^[75]通过设计 Cd^{2+} 和 Pb^{2+} 阳离子混合玻璃系统，并利用飞秒激光诱导相分离技术实现了 PQDs 的相组成和带隙的调控(见图 2e)，得到了 461~520 nm 处的可调发射(见图 2f)。除此之外，所制备的 $\text{CsCd}_x\text{Pb}_{1-x}\text{Br}_3$ PQDs 在 467 nm 处纯蓝色发光的光致发光量子产率达到 13.4%，是 $\text{CsPb}(\text{ClBr})_3$ PQDs 的 2 倍。



S_{PA} to S_{PG} represent the $\text{CsPb}(\text{Br}_{1-x}\text{I}_x)_3$ PQDs written in glass with different laser parameters.

图 2 飞秒激光调控玻璃内部钙钛矿量子点的析晶类型^[74-75]

Fig. 2 Femtosecond laser controls the crystallization type of PQDs in glass^[74-75]

1.3 增强析晶能力

CsPbX_3 量子点在玻璃基质中的析出一方面需

要外界给予一定的能量如热场或者机械应力等去打破析晶势垒，另一方面也需要前驱体玻璃对钙钛矿

组成元素尤其是不同种卤素具备较高的溶解能力。一般来说, 对于一些玻璃网络结构较为紧密的体系如硼硅酸盐等, 比较难析出蓝色发射的 $\text{CsPb}(\text{Br}/\text{Cl})_3$ 或 CsPbCl_3 量子点, 那是因为在其对卤素的溶解度较低, 且玻璃熔制过程中卤素挥发过多, 导致前驱体玻璃很难通过热场或者机械应力等方式去诱导析出钙钛矿量子点。而选择网络结构疏松的磷酸盐体系去制备全色 CsPbX_3 量子点玻璃又存在稳定性低的风险。基于此, Huang 等^[76]发现在

硼硅酸盐体系中, 使用飞秒激光辐照后结合低温热处理可以在玻璃内部中析出 $\text{CsPb}(\text{Br}/\text{Cl})_3$ 量子点。然而正常热场处理是无法使其析晶的, 这是由于飞秒激光辐照导致玻璃网络的局部断裂, 进而促进原子迁移和重排形成晶核, 降低了钙钛矿量子点的析晶壁垒, 如图 3 所示。并且制备的在玻璃内部的 $\text{CsPb}(\text{Br}/\text{Cl})_3$ 图案具有很好的抗湿和氧稳定性。这一发现对钙钛矿量子点玻璃的制备具有重大指导意义。

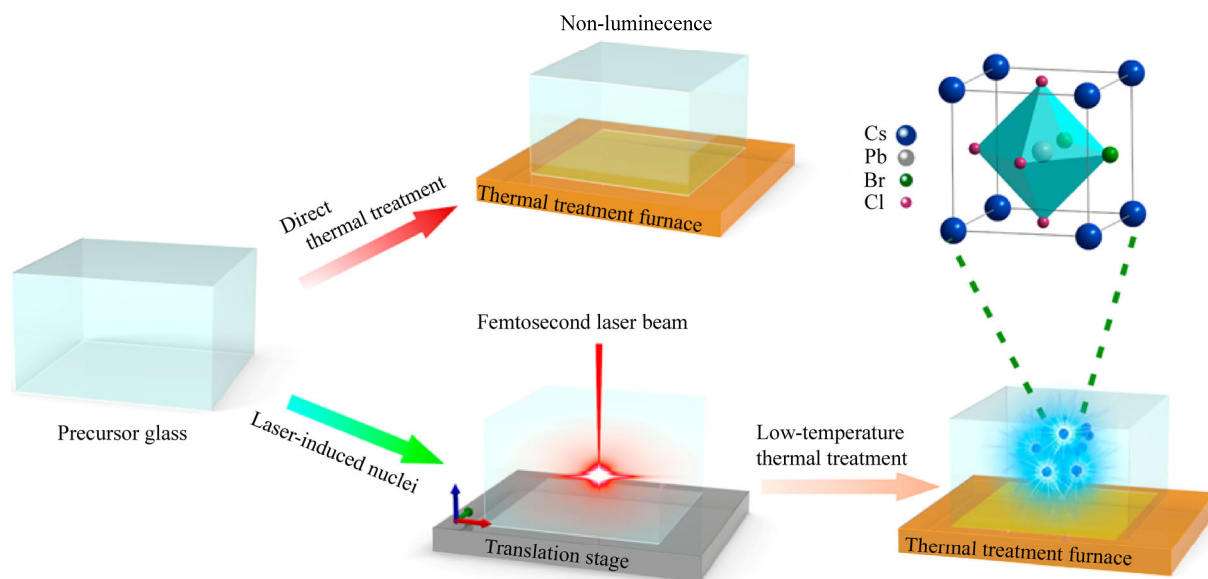


图 3 飞秒激光诱导玻璃内部局部形成 $\text{CsPb}(\text{Cl}/\text{Br})_3$ 量子点的示意图^[76]

Fig. 3 Schematic illustration of the femtosecond laser induced formation of $\text{CsPb}(\text{Cl}/\text{Br})_3$ PQDs inside glass in a localized fashion^[76]

2 飞秒激光调控钙钛矿量子点玻璃的光学性能研究进展

飞秒激光不但可以通过非线性吸收与钙钛矿量子点前驱体玻璃相互作用诱导析晶, 还可以通过 3D 位移平台实现钙钛矿量子点的阵列化, 赋予 CsPbX_3 量子点一定的偏振特性。除此之外, 飞秒激光作为一种高功率的激发源, 直接与玻璃中的 CsPbX_3 量子点相互作用, 也可以实现一些特殊的光学性能。

2.1 可逆发光

钙钛矿量子点由于其形成能低和独特的离子晶体结构, 易受到外界环境因素如强光、高温或高湿环境下发生分解。由于玻璃的包覆, 钙钛矿量子点具有出色的物化稳定性, 在高温高湿环境下依旧保持良好的光学性能。然而, 钙钛矿量子点玻璃由于具有较高的透过率, 在强光照下, 钙钛矿量子点的光学性能易受到影响。基于此, Huang 等^[50, 76]利

用飞秒激光辐照已经析晶的钙钛矿量子点玻璃, 发现在较低功率飞秒激光下, 钙钛矿量子点的发光产生猝灭, 并且可以通过低温热处理恢复其发光, 如图 4a 所示。而且通过飞秒激光擦除的钙钛矿量子点的发光强度通过热处理后能完全恢复, 这表明在飞秒激光作用下, 钙钛矿量子点的发光是完全可逆的(见图 4b~图 4c)。低功率飞秒激光作用下, 已形成的钙钛矿量子点部分重新“溶解”进玻璃网络中, 从而导致表面产生大量缺陷。由于强的声子-声子耦合效应, 钙钛矿量子点的发光猝灭。擦除-恢复机理如图 4d 所示, 因为量子点只是部分的被分解, 并且其组成元素仍保留在玻璃网络中, 因此, 在低温热处理下, 钙钛矿量子点的结构和缺陷很容易进行修复, 从而实现了飞秒激光辐照和低温热处理操控玻璃中钙钛矿量子点的可逆发光和发光信息的重复写入擦除(见图 4e)。基于此, 实现了三维光学信息可擦除化, 扩展了在三维显示、信息防伪和光学信息存储领域的应用。

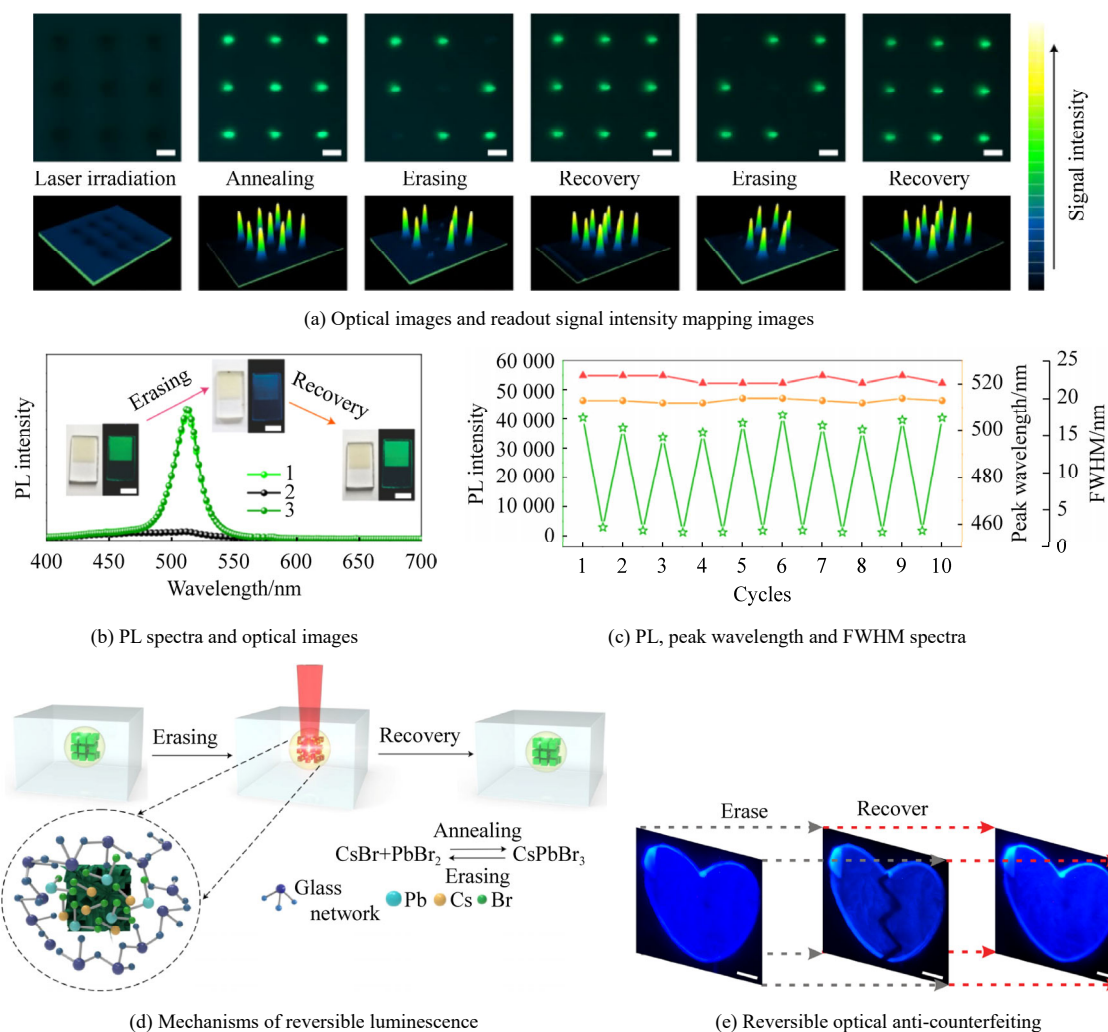


图4 飞秒激光实现钙钛矿量子点玻璃的可逆发光性能^[50, 76]
Fig. 4 Reversible luminescence of PQDs embedded glass achieved by femtosecond laser^[50, 76]

2.2 偏振发光

CsPbX₃ 量子点为立方晶相，在室温下具有较高的对称性，因此在单晶和胶体溶液中几乎不存在光学各向异性。Zhou 等^[77]发现 CsPbX₃ 纳米线在不同方向上的定向重组可以赋予其偏振发射特性，在不同极化激发下，由于不同极化角度下光致发光强度的差异，防伪图案会呈现出不同的图案。虽然上述方法可以赋予钙钛矿量子点偏振发射特性，但实现其定向排列的过程相对复杂，尤其难以适用于复杂的防伪图案。Chen 等^[78]利用飞秒激光结合热处理在钙钛矿前驱体玻璃中生成线阵列结构，如图 5a 所示。制备的钙钛矿量子点的线阵列具有极化度高达 0.189 的极化发射，如图 5b 所示。基于此，利用钙钛矿量子点线阵列可以通过编程设计转换成图案，在不同偏振角度下具有偏振防伪特性，将高空间分辨率的激光加工与透明玻璃的三维空间相结合，可以构建具有发光各

向异性的多层钙钛矿量子点图案，用于三维模式下的光学防伪(见图 5c~图 5d)。更重要的是，由于无机玻璃基体的保护，钙钛矿量子点线阵列组成的三维偏振发射结构在水中可以很好地保存。该策略为其他各向同性或各向异性材料的极化特性生成提供了一个通用平台，为加工不同防伪图案的高精度智能防伪设备的设计和制造打开了新的大门。

2.3 放大自发辐射与随机激光输出

钙钛矿量子点是优秀的光增益材料，将钙钛矿量子点与各种光学共振腔结合能够实现低阈值的激光输出^[13, 79]。对于稳定性和发光效率兼备的 CsPbBr₃ 量子点玻璃而言，CsPbBr₃ 量子点在玻璃中均匀分布使其适合作为无序的增益介质实现激光输出。Liu 等^[80]在硼硅酸盐玻璃中制备了 CsPbCl₂Br 量子点，如图 6a 所示。并首次在室温下利用 800 nm 飞秒激光激发下观察到了放大自发辐射(ASE)现象，

如图 6b 所示。并且随着热处理温度在 530 °C 时, ASE 的阈值低至 0.19 mJ/cm^2 , 为钙钛矿量子点玻璃的激光应用提供了新的策略(见图 6c~图 6d)。Yuan 等^[49]在硝酸盐玻璃中制备的 CsPbBr_3 量子点中均匀分布而且具有优良的稳定性, 量子效率高达 70%, 并利用 800 nm 飞秒激光作为激发源实现了随机激光输出, 如图 6e 所示。随着泵浦功率的增大,

CsPbBr_3 量子点玻璃的发射峰出现 1 个半峰宽小于 1 nm 的尖峰, 继续增大飞秒激光的功率, 光谱出现更多尖峰, 说明 CsPbBr_3 量子点玻璃可以实现随机激光输出, 阈值为 $200 \mu\text{J/cm}^2$, 如图 6f 所示。而由于玻璃中量子点的随机分布, 散射强度不同导致在不同角度测试的随机激光光谱也存在差异, 如图 6g~图 6h 所示。

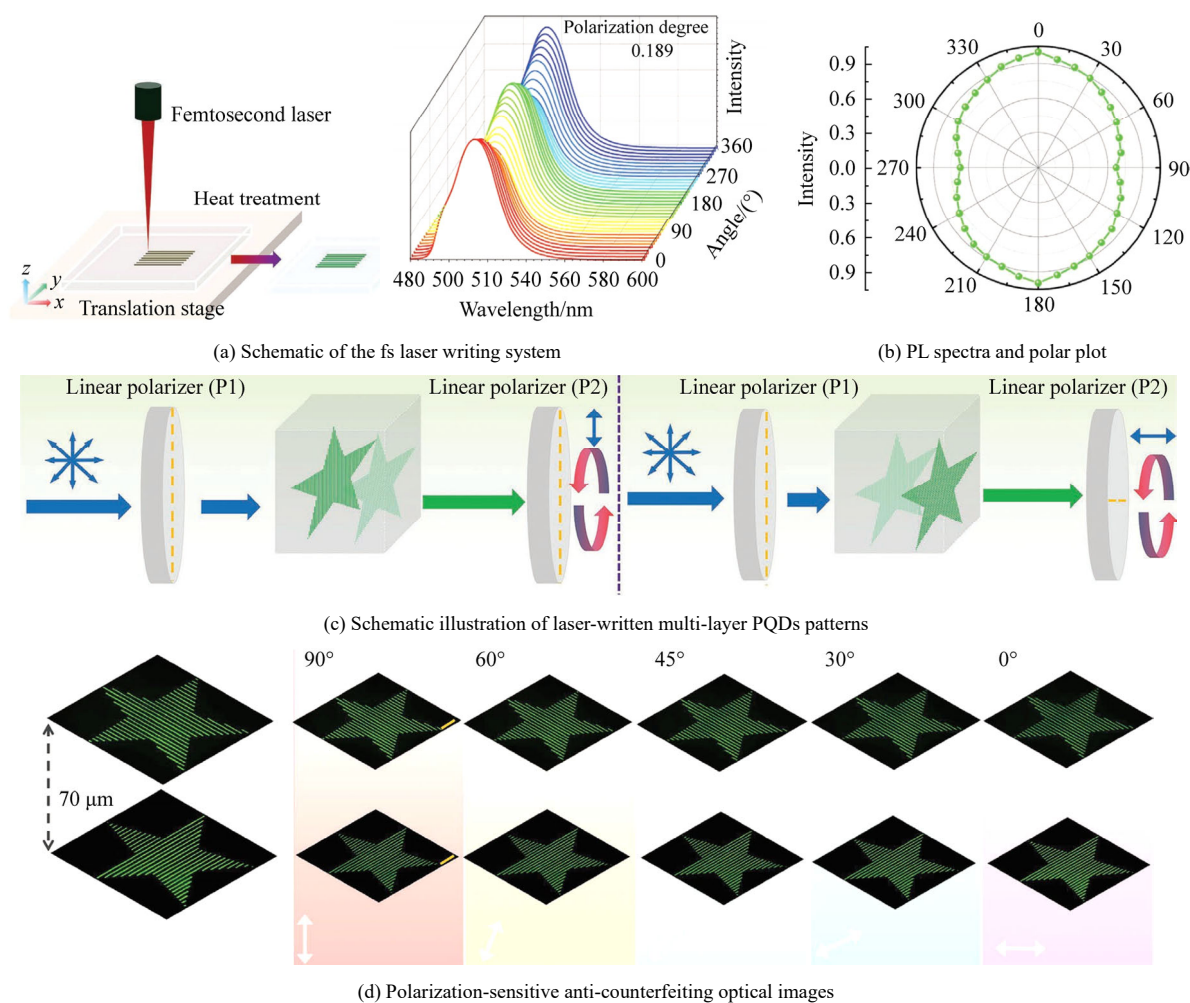


图 5 飞秒激光实现钙钛矿量子点玻璃偏振发光性能^[78]

Fig. 5 Polarization luminescence of PQDs embedded glass achieved by femtosecond laser^[78]

然而, CsPbBr_3 量子点玻璃必须在低温(77 K)环境下才能实现随机激光输出,这是由于低温抑制了电子-声子耦合所引起的非辐射跃迁。目前,钙钛矿量子点玻璃在常温下仍难以实现激光输出。主要有以下 3 个原因: 1) 由于玻璃网络结构的紧密,钙钛矿量子点在成核和生长过程中受到限制,其结晶度不够完整; 2) 玻璃中钙钛矿量子点的浓度难以提高,导致所提供的光增益不够; 3) 玻璃内部难以实现良好的光学共振腔,使钙钛矿量子点很难实现粒子数反转。因此,进一步优化玻璃组分以提高钙钛

矿量子点的结晶度和浓度,或将钙钛矿量子点玻璃制备成光学微球或玻璃光纤有望降低激光输出阈值,实现常温状态下高质量单模激光输出仍具有重大意义。

2.4 长余辉发光

超快激光已被用于在透明固体中制造三维功能结构^[50], 飞秒激光与透明介质相互作用时,通过非线性电离将能量传递给电子,并且被电子吸收的部分光能在皮秒时间尺度上转移到晶格中。由于脉冲持续时间短于电子到晶格的能量转移持

续时间,形成了相应材料的亚稳态结构,作为俘获中心,从而有助于实现长余辉发光(LPL)性能^[81]。Qiu等^[82]在 Ln^{3+} ($\text{Ln}=\text{Ce}, \text{Tb}$ 或 Pr)掺杂玻璃中观察到了飞秒激光照射的 LPL,在黑暗中即使肉眼也能清晰地看到发光。此外,利用飞秒激光,研究者们成功在 Eu^{2+} 掺杂铝硅酸盐玻璃^[82]、锆硅酸盐玻璃^[83]和 Mn^{2+} 掺杂的氟化物玻璃^[84]中实现了

LPL 性能。

利用飞秒激光作用钙钛矿量子点玻璃造成缺陷,为探索其室温长余辉性能提供了一种有效途径。基于此,Peng等^[85]成功利用飞秒激光作用钙钛矿量子点玻璃实现了长余辉性能。他们利用聚集后的飞秒激光辐照已经析晶的 CsPbBr_3 玻璃,如图7a所示;随后可以观察到 CsPbBr_3 玻璃的长

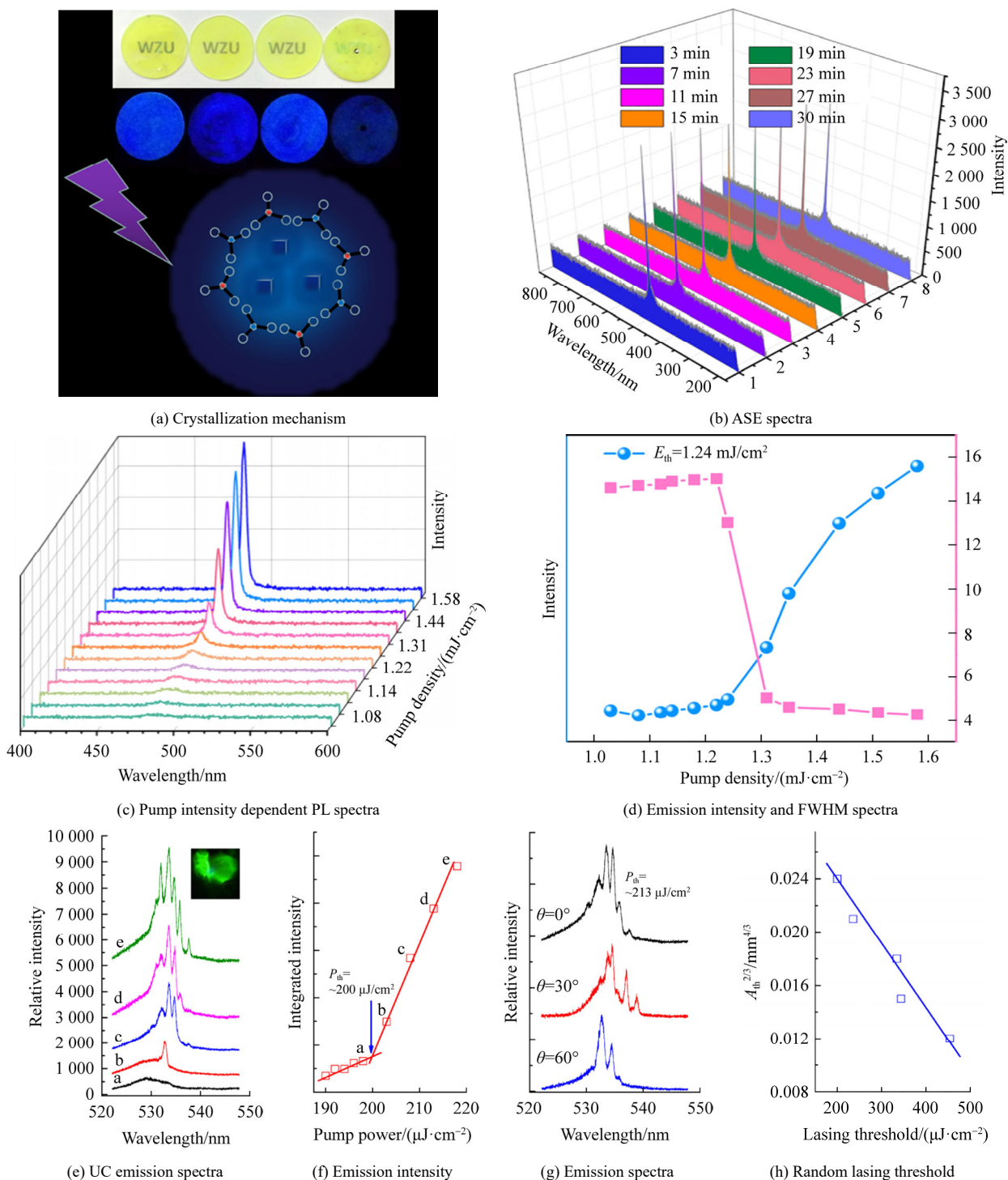
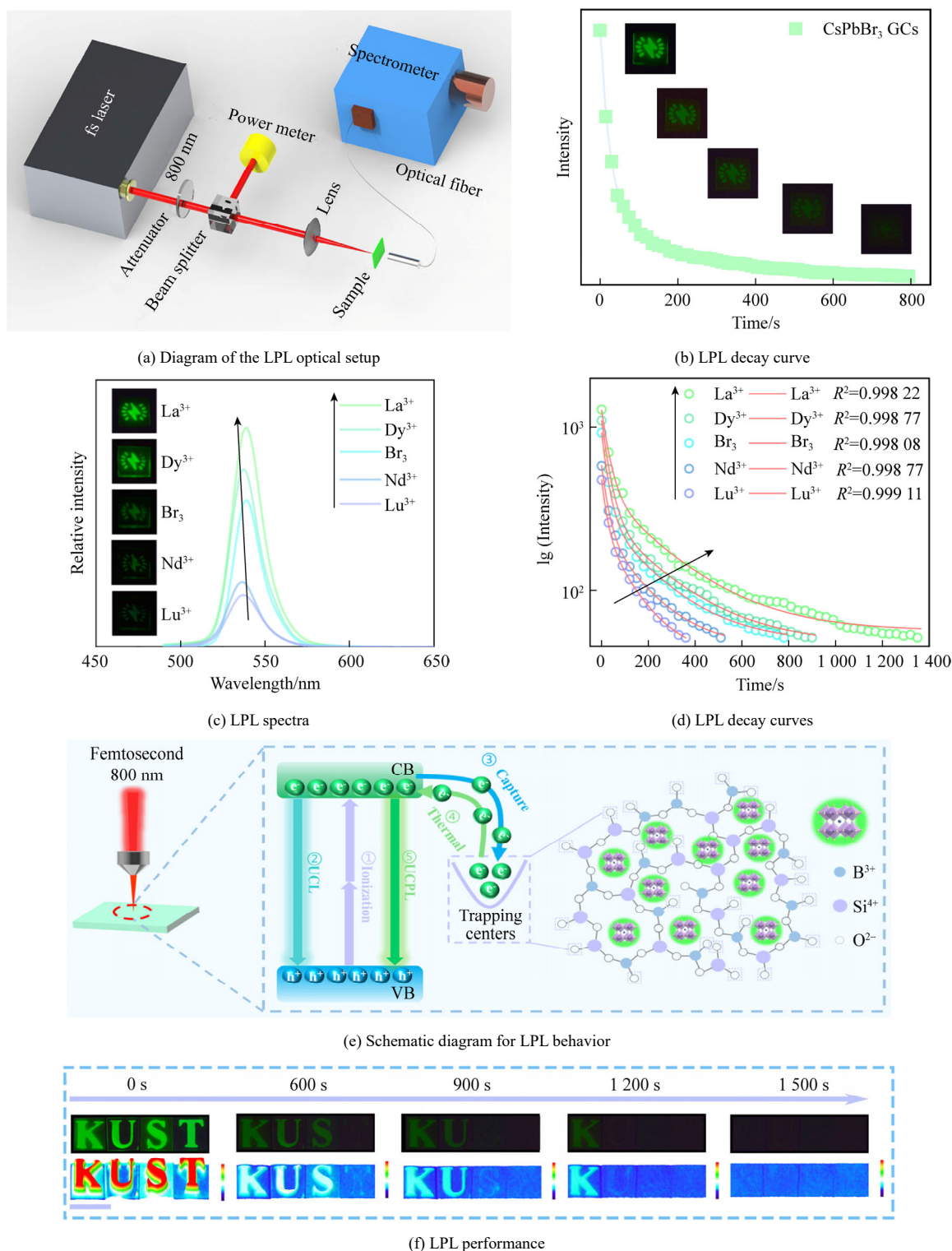


图6 飞秒激光实现钙钛矿量子点玻璃放大自发辐射与激光输出性能^[49, 80]

Fig. 6 Amplified spontaneous emission and laser of PQDs embedded glass achieved by femtosecond laser^[49, 80]

图 7 飞秒激光实现钙钛矿量子点玻璃长余辉性能^[85]Fig. 7 Long persistent luminescence of PQDs embedded glass achieved by femtosecond laser^[85]

余辉发光,如图 7b 所示。此外,通过镧系离子(La^{3+} 、 Dy^{3+} 、 Nd^{3+} 和 Lu^{3+})掺杂实现了对陷阱的操纵,使室温下 LPL 时间的调节范围从 350 s 到 1350 s 不等,如图 7c~图 7d 所示。这是由于飞秒激光辐照后在玻璃基体中形成了一种作为俘获中心的氧空位。如

图 7e 所示,在 800 nm 飞秒激光的照射下,价带的电子被双光子吸收激发到导带,然后被激发的电子与空穴复合,形成发射波长为 540 nm 的上转换发光过程。同时,高能 800 nm 飞秒激光照射下,玻璃基体的非桥氧键被破坏,形成俘获中心。另外,自

由载流子通过多光子电离、局域加热和碰撞电离等过程在玻璃基体中形成, 这些自由载流子可以被形成的俘获中心捕获。因此在去除飞秒激光后, 室温热扰动诱导的载流子释放形成绿色 LPL。最后如图 7f 所示, 实现了相关 LPL 性能的防伪演示, 且具有可重写、高色纯度和可调 LPL 等优异的光学性能, 为构建下一代光学防伪和光存储器件提供了新的思路。

3 总结与展望

将钙钛矿量子点包覆在透明玻璃介质中, 极大程度的提高了稳定性的同时还保持了良好的光学性能, 近年来受到研究者的广泛关注。利用飞秒激光可以在三维空间内调控钙钛矿量子点玻璃的析晶行为, 对三维光学信息加密存储领域具有重大意义。此外, 利用飞秒激光与钙钛矿量子点玻璃的相互作用, 还可以实现可逆发光、激光、偏振与长余辉等光学性能, 极大的扩展了钙钛矿量子点玻璃的应用领域。但飞秒激光与钙钛矿量子点玻璃方向仍有很多值得广大研究者们探究解决的问题: 利用飞秒激光在玻璃中制备钙钛矿波导或者单晶, 有望赋予无机玻璃光电性能; 利用飞秒激光设计制备无铅钙钛矿玻璃, 在保持无毒高光学性能的前提下进一步探究其光学应用; 利用飞秒激光作为泵浦源, 在室温下实现钙钛矿量子点玻璃的激光输出; 设计特定光学设备和原理, 使飞秒激光在玻璃内部刻写的钙钛矿量子点进一步缩小到纳米尺度, 极大程度提高三维光学信息存储量等。相信在不久的将来, 飞秒激光作用下的钙钛矿量子点玻璃将带领我们进军一个崭新的光电世界。

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Research Progress in Crystallization and Optical Properties of Perovskite Quantum Dot Glass Regulated by Femtosecond Laser

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Extended Abstract

All-inorganic cesium lead halide (CsPbX₃, X = Cl, Br, I) perovskite quantum-dots (PQDs) glass exhibits exceptional optical and electrical properties, such as high quantum yield (QY), high purity, tunable emission wavelength, high defect tolerance, and fast charge carrier diffusion rates, making them promising for a wide range of applications in photovoltaics, light-emitting diodes (LEDs), photodetectors, lasers, and other optoelectronic devices. However, perovskite quantum dots are prone to degradation due to their ionic

structure and high surface energy when exposed to circumstances of oxygen, moisture, high temperatures, and intense light. In order to enhance their stability and maintain the high luminescence efficiency, researchers have begun to incorporate these CsPbX_3 quantum dots into high-transparency glass substrates with excellent thermal, mechanical, and chemical stability. In recent years, many researchers have successfully synthesized PQDs embedded glass systems such as silicate, germanate, tellurite, phosphate, and borate, and have applied the synthesized material in fields of optical sensing, X-ray imaging, lasers, optical information storage, and optical anti-counterfeiting.

Common methods to prepare PQDs embedded glass include melt-quenching method, mechanical stress-induced method, and water-induced methods. Both thermal treatment methods fail to localize crystallization, while stress- or water-induced crystallization detrimentally affect the glass structure and introduce toxicity from surface heavy metal Pb, significantly limit their application prospects. Fortunately, ultra-short pulse laser, femtosecond laser processing of transparent materials, has been demonstrated as an effective means to construct three-dimensional photonic device structures. This facilitates the materials to be hopefully applied in nonlinear optics, optical data storage, and nanophotonics. Femtosecond laser interacts with transparent materials via multiphoton absorption, circumventing the need to consider material absorption or introduce new absorption centers, and the highly localized energy of focused ultra-short pulse laser is achieved. The high spatial resolution of this processing is realized by the rapid redistribution of atoms at the laser focus induced by successive nonlinear optical processes. This technique has been successfully applied to introduce microcracks, alter micro-zone refractive indices, and form nanocrystals. Compared to traditional methods for preparing perovskite quantum dots, femtosecond laser is more suitable for precipitating perovskite quantum dots within transparent glass materials.

This article provides a comprehensive overview of the progress made in studying the crystallization and optical properties of CsPbX_3 PQDs embedded glass under femtosecond laser irradiation, and offers new ideas and insights for future research and application of PQDs embedded glass regulated by femtosecond laser.

Summary and prospects Coating PQDs in transparent glass media has greatly enhanced stability while maintaining excellent optical properties, so as to attract widespread attention from researchers in recent years. Utilizing femtosecond laser technology enables the manipulation of crystallization behavior of perovskite quantum dot glass in three-dimensional space, which holds significant implications for three-dimensional optical information encryption and storage. Additionally, the interaction between femtosecond laser and PQDs embedded glass enables reversible luminescence, laser emission, polarization, and long persistent luminescence properties, significantly expanding the application domains of PQDs embedded glass. However, many challenges still exist in the direction of femtosecond laser and PQDs embedded glass that researchers need to explore and resolve. The challenges are: how to use femtosecond laser to fabricate perovskite waveguides or single crystals in glass, potentially endowing inorganic glass with optoelectronic properties; how to design and to fabricate lead-free perovskite glass using femtosecond laser to further investigate its optical applications while maintaining non-toxic high optical performance; how to utilize femtosecond laser as pump sources to achieve laser output from PQDs embedded glass at room temperature; how to design specific optical devices and principles to further reduce the size of PQDs written inside glass to the nanometer scale using femtosecond laser, which is expected to greatly enhance the three-dimensional optical information storage capacity, etc. It is believed that in the near future, PQDs embedded glass under the influence of femtosecond lasers will lead us into a brand-new optoelectronic world.

Keywords perovskite quantum dots; glass; femtosecond laser