可溶液加工纳米光电材料与器件

刘洋, 朱阳斌, 马福民, 郑悦婷, 胡海龙, 郭太良, 李福山*

福州大学物理与信息工程学院, 福州 350108

* 联系人, E-mail: fsli@fzu.edu.cn

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摘要 光电器件的柔性化、结构微型化是光电技术发展的重要趋势. 溶液法加工特别是印刷技术和纳米光电材料的结合, 有利于克服传统光电器件制备工艺复杂、成本高昂的局限性, 在未来柔性化、图案化以及大面积光电器件领域具有广阔的应用前景. 本文主要聚焦于可溶液加工纳米光电材料与器件, 介绍了我们课题组近年来在该领域的科研进展, 包括喷墨打印量子点技术与应用, 溶液加工量子点界面发光机制, 以及发光、探测、突触器件结构设计及性能优化, 希望为该领域学术研究和产业应用提供参考.

关键词 光电器件, 溶液加工技术, 纳米光电材料, 钙钛矿

自古以来, 人类一直在寻求低成本的信息传播和产品生产的方式. 近2000年前, 中国四大发明之一印刷术的出现为知识信息的系统积淀和广泛传播创造了极大便利, 是人类文明史上的光辉篇章. 近50年来, 半导体硅材料和微纳加工技术得到长足的发展, 形成了极其复杂的技术体系, 在光电领域占据绝对的主导地位. 但是, 随着人们对光电产品需求的日益旺盛以及光电器件结构朝着微型化发展, 传统半导体器件制备工艺复杂、成本高昂的局限性愈加明显, 阻碍了该领域的长远发展^[1]. 纳米光电材料可以通过表面修饰稳定分散在溶液中^[2~5], 或者以液相前驱体形式存在^[6~8], 然后以溶液法加工的方式沉积形成所需薄膜或图案, 提供了一种替代传统复杂半导体制备工艺的简单路径. 近20年来, 纳米材料取得了长足进步, 量子点^[9,10]和钙钛矿^[11~13]为代表的纳米光电材料以优异的荧光量子产率、高色纯度、光谱随成分粒径简单可调及便于溶液法成膜等优势, 在光电器件领域展现出诱人的应用前景^[14~17]. 将源远流长的溶液印刷技术及纳米材料应用

于光电器件领域, 是实现光电器件低成本生产的重要途径, 同时也是我国摆脱西方核心技术垄断, 实现光电领域弯道超车的历史机遇, 对我国光电产业的发展具有重要的战略意义.

1 量子点发光材料与应用

1.1 喷墨打印量子点发光技术与应用

喷墨打印是一种定向沉积的数字化溶液加工技术, 具备低成本、大面积和图案化的天然优势, 可以很好地与纳米光电材料匹配, 在发光显示等领域具有潜在的产业化应用价值^[14,16,18~26]. 目前, 喷墨打印量子点存在成膜不均一的问题, 这是制约喷墨打印在量子点发光显示领域发展的重要原因. 因此, 从墨滴蒸发及其伴随的流体动力学来理解和调控量子点输运实现均匀成膜, 对于基础科学研究及应用产业化都有重要意义.

基于此, 我们根据量子点发光二极管(quantum dot light emitting diode, QLED)器件的要求, 设计了以导电

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聚合物poly(*N,N'*-bis-4-butylphenyl-*N,N'*-bisphenyl)benzidine(poly-TPD)作为空穴传输层的正置器件结构。在此基础上,配制了一系列稳定分散且不破坏空穴传输层的多组量子点墨水,研究了空穴传输层上的均一化墨水输运及量子点自组装的机理,证明了高黏度、大接触角和小接触角滞后有利于量子点输运形成均匀致密的薄膜,如图1(a)和(b)^[27]。我们发现,墨滴在接触角低于10°时,依然呈现出三相接触线滑移和量子点输运自

组装过程。我们利用调控量子点薄膜形态的策略,成功地在poly-TPD层上打印了均匀且光滑致密的量子点薄膜,如图1(b)。在喷墨打印的高质量量子点薄膜的基础上,制备出基于正置结构的全溶液法QLED,如图1(c)。在4.0 V偏压下,器件表现出很好的电致发光均匀性,没有发光坏点,如图1(d)。喷墨打印QLED的开启电压低至2.0 V,亮度在6 V电压下增加到约2000 cd/m²,在12 V电压下达到12100 cd/m²。器件在1974 cd/m²亮度下

图 1 (网络版彩色)喷墨打印QLED^[27]. (a) 像素基板上喷墨打印量子点示意图; (b) 基于复合溶剂的量子点墨水均匀成膜的荧光显微镜图(标尺为100 μm), 以及放大的荧光显微镜图(标尺为20 μm); (c) 器件结构示意图; (d) 电致发光显微镜图; (e) 电流密度-亮度-电压(*J-L-V*)特性; (f) 电流效率-电流密度曲线, 插图为QLED电致发光光谱

Figure 1 (Color online) Inkjet-printed QLED^[27]. (a) Schematic of inkjet printing quantum dots (QDs) on pixelated substrates; (b) photoluminescence (PL) microscopic images of homogeneous dots array with mixture of solvents (the scale bar is 100 μm); and its enlarged pattern (the scale bar is 20 μm); (c) schematic of the inkjet-printed QLED; (d) electroluminescence microscope image; (e) current density-luminance-voltage (*J-L-V*) characteristics; (f) current efficiency-current density curve, the inset is the electroluminescence spectrum of the QLED

实现最大电流效率4.44 cd/A, 如图1(e)和(f). 该结果将为印刷QLED显示溶液法制备高质量像素提供重要借鉴.

在自然环境中, 微米尺度的墨滴滴落在基板上是一个固-液-气三相共存并经历蒸发、输运、干燥、成膜多个阶段的复杂系统; 这些过程具有较强的环境敏感性, 容易受到外界温度、表面气流、压力和基板匀质性的影响, 因此很难处于一种平衡状态^[28]. 特别是当墨滴含有纳米材料时, 该过程更加复杂多变. 虽然这种复杂性对于传统的薄膜光电器件是缺点, 但是在不可复制、低成本、图案化领域具备潜在应用价值, 比如防伪标签^[29~34].

基于此, 我们以商业化的锡化镉(CdSe)量子点为例, 研究了微尺度量子点墨水的差异化输运与自组装机理, 成功沉积了不可复制的量子点荧光图案, 并探究了其在不可复制防伪标签中的应用^[35]. 首先, 将CdSe核-壳量子点分散于高沸点的溶剂中作为打印墨水, 以降低墨水的相变速率, 同时增加墨水输运在蒸发过程中对环境的敏感性. 进一步, 在基板表面构建具有随机分布的聚甲基丙烯酸甲酯(poly methyl 2-methylpro-

penoate, PMMA)微纳米颗粒, 作为喷墨打印输运过程中的聚集钉扎点, 强化输运过程中的差异性. 量子点墨滴在外界环境和钉扎点牵引力的共同作用下, 随机沉积在钉扎点附近, 形成物理不可克隆的“花状”图案, 如图2(a)~(c). 利用喷墨打印技术可以制备多种复杂的宏观荧光图像, 如图2(d). 不同批次的荧光图案在宏观水平是相同的; 然而, 在微观层面上, 每个荧光点彼此各不相同, 即相同条件下无法进行伪造, 大大增加了防伪的安全性. 这些微观图案可以通过便携式的手机显微镜来拍照识别, 如图2(e). 最后, 我们引入了人工智能识别技术(特别是深度学习), 实现对喷墨打印防伪标签的识别和验证, 并成功地识别不同清晰度、亮度、旋转角度、放大倍率以及混合这些参数的“花状”图片, 如图2(f). 该结果可以丰富喷墨打印的输运理论, 同时为未来低成本纳米发光材料智能防伪标签的研究提供重要创新思路.

1.2 量子点界面发光机制

量子点界面对量子点的发光特性有着显著的影响,

图2 (网络版彩色)喷墨打印量子点的差异化输运与防伪应用^[35]. PMMA膜上修饰随机分布的PMMA纳米颗粒钉扎点(a), 喷墨打印量子点墨水及输运过程(b), 和形成的不可复制花状图案(c)示意图. 喷墨打印宏观图案(d)及其微观放大图(e); (f)深度学习进行标签验证的示意图

Figure 2 (Color online) Differential transportation and anti-counterfeiting application of inkjet-printing QDs^[35]. Schematics illustrating substrate modification with random-distributed pinning points of PMMA nanoparticles on PMMA film (a), inkjet printing of QDs ink and corresponding transportation process (b), and obtained unclonable flower-like dot patterns (c). Fluorescence images of inkjet-printed macroscopic patterns (d), and its corresponding enlarged image (e). (f) Schematic of authenticating process with deep learning technique

包括荧光效率、缺陷密度、能级匹配等^[5]。目前,关于量子点薄膜界面处的能带渐变和光学带隙调制鲜有研究。可溶液法加工的钙钛矿薄膜和钙钛矿量子点由于其特有的晶体结构和光电特性,在光电器件领域显示出巨大的应用前景,因此,其卤素阴离子动态特性对于钙钛矿界面发光特性无疑是至关重要的^[12,36-39]。

鉴于此,我们设计了 $\text{CH}_3\text{NH}_3\text{PbI}_3$ 薄膜和 CsPbBr_3 量子点的复合界面,实现了固体界面处的可控卤素阴离子交换,如图3(a)^[40]。沉积在 $\text{CH}_3\text{NH}_3\text{PbI}_3$ 薄膜上的 CsPbBr_3 量子点,其发光颜色由最初的绿色逐渐过渡到红色(522~650 nm),表明实现了对量子点薄膜的带隙调控,如图3(b)和(c)。离子交换反应过程中, $\text{CH}_3\text{NH}_3\text{PbI}_3$ 薄膜和 CsPbBr_3 量子点的形态都得到了很好的保留。此外,通过调节 CsPbBr_3 量子点表面的配体油胺和油酸的密度,可以调节 CsPbBr_3 量子点与 $\text{CH}_3\text{NH}_3\text{PbI}_3$ 薄膜之间的阴离子交换过程,使得离子交换反应过程可以持续数百至数千秒。我们进一步构建了 $\text{CH}_3\text{NH}_3\text{PbI}_3$ 微米网络和 CsPbBr_3 量子点复合结构。微米网络表面的 CsPbBr_3 量子点与 $\text{CH}_3\text{NH}_3\text{PbI}_3$ 薄膜充分接触,发生了离子交换而出现颜色变化;同时,微米网络缝隙中的 CsPbBr_3 量子点保持原有绿色。这一在微纳尺度上的差异化颜色和形态现象,意味着该复合结构可以用于图

案化光电器件以及不可重复多彩的防伪标签。

1.3 量子点发光器件结构设计与性能优化

QLED被认为是下一代高质量显示和固态照明的理想选择。在过去的十几年中,科学家们已经进行了大量QLED相关的研究以改善器件性能,并探索大面积器件的制造工艺^[41-43]。在QLED的多层结构中,无机氧化锌(ZnO)纳米颗粒被广泛用作电子传输层,它具有很高的电子迁移率($2 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)^[44]。聚(3,4-乙烯二氧噻吩)-聚苯乙炔磺酸(PEDOT:PSS)是使用最广泛的空穴注入层材料^[45]。但是, PEDOT:PSS具有以下缺点: (1) PEDOT:PSS的功函数比较小,不利于空穴有效注入; (2) PEDOT:PSS的水溶液具有很大的表面张力,对于大规模制造(如喷墨印刷),不利于形成均匀的膜。为了解决上述问题,有课题组尝试用无机金属氧化物氧化镍(NiO)和氧化钨(WO_3)等来代替PEDOT:PSS^[46,47]。然而,使用无机金属氧化物作为空穴注入层仍存在很多问题。金属氧化层通常需要在高温下使用真空热蒸发沉积,或使用旋涂工艺后进行高温退火,这种高温工艺不利于器件性能,并且无法兼容QLED的重要应用——柔性显示。此外,目前基于无机材料作为空穴注入层的QLED性能远低于预期^[45]。

图3 (网络版彩色) $\text{CH}_3\text{NH}_3\text{PbI}_3$ 薄膜和 CsPbBr_3 量子点固态界面离子交换^[40]。(a)示意图;(b)随时间变化的光致发光图片;(c)原位PL谱
Figure 3 (Color online) Ion exchange in the interface of CsPbBr_3 QDs and $\text{CH}_3\text{NH}_3\text{PbI}_3$ film^[40]。(a) Schematic diagram; (b) PL images with time; (c) In-situ PL spectra

为了解决这些问题,我们报道了一种基于有机-无机杂化空穴注入层的QLED器件,如图4所示.该器件采用掺杂无机氧化钼 MoO_x 的PEDOT:PSS作为空穴注入层.通过这种方法,空穴注入层的费米能级从4.9 eV增加到5.3 eV,为器件提供了更好的能级匹配以提高空穴注入能力^[48],器件性能显著提升,最大电流效率为18.6 cd/A,峰值外量子效率为18.2%,比未掺杂的器件性能提升约1.5倍(12.7 cd/A和12.3%).更令人兴奋的是,PEDOT:PSS铺展性差的问题在透明导电氧化物 MoO_x 掺杂后得到了大大改善.通过掺杂 MoO_x ,降低了PEDOT:PSS水溶液的表面张力,使其与喷墨打印工艺相兼容.通过喷墨打印PEDOT:PSS的QLED表现出高性能,其峰值外量子效率为13.1%.我们的研究表明,有机-无机杂化的空穴注入层可能为大面积高性能QLED的制造提供一种新的思路.

2 光敏感钙钛矿纳米器件

2.1 喷墨打印钙钛矿光探测器

光电探测器可以将入射光子信号转换为电信号,有广泛而重要的应用,比如光通信、环境监测、安全监视和化学/生物传感^[49-52].在过去的几十年中,多种类型的半导体材料已经被应用于光电探测器,例如Si、ZnO、量子点和聚合物.近年来,复合钙钛矿材料 $\text{CH}_3\text{NH}_3\text{PbI}_3$ 凭借其简单的溶液法制备工艺以及优异的光电特性,在太阳能电池领域取得了令人瞩目的成

果^[53-56].同时, $\text{CH}_3\text{NH}_3\text{PbI}_3$ 合适的光学带隙、较高的吸光系数、较大的载流子迁移率以及较长的激子扩散长度等光电特性^[53]也有助于实现高效的光电探测器.

由于钙钛矿 $\text{CH}_3\text{NH}_3\text{PbI}_3$ 前驱体为强极性溶剂,并且成膜过程涉及晶体的结晶,因此在溶液加工过程中,相关的输运和组装过程与量子点相比具有一些独特的性质.此外,目前报道的基于钙钛矿材料的光电器件大多限于旋涂等传统溶液法成膜工艺,限制了钙钛矿在大面积和阵列化光电器件领域的应用.喷墨打印方法沉积钙钛矿 $\text{CH}_3\text{NH}_3\text{PbI}_3$ 是一个有潜力的解决方案.但是,基于喷墨打印技术的溶液法成膜工艺,其墨滴蒸发速度慢且不均匀,导致钙钛矿薄膜不致密、不均匀,限制了喷墨打印在该领域的应用.

基于此,我们研究了喷墨打印过程中钙钛矿材料的墨水蒸发输运,以及伴随的晶体取向生长特性,并探索了其光电探测应用.结果表明,通过溶剂工程调控晶体生长取向,并通过晶体生长速率实现钙钛矿晶体尺寸形貌的控制,成功地利用喷墨打印工艺制备了复合钙钛矿 $\text{CH}_3\text{NH}_3\text{PbI}_3$ 纳米线、微米线、纳米网络和岛状结构薄膜,如图5(a)和(b)^[53].基于这些薄膜覆盖率低的钙钛矿晶体,我们设计了电极-沟道-电极的平面型结构,其中,基于钙钛矿微米线的光电探测器实现了薄膜高覆盖和晶体低缺陷性的平衡;该器件在光功率密度为 0.1 mW/cm^2 的光激发下,获得了16000%的开关比、 1.2 A/W 的响应度和 2.39×10^{12} Jones的归一化探测率,如图5(c).基于钙钛矿微米线的光电探测器阵列可以应

图4 (网络版彩色)基于复合空穴注入层的QLED器件结构及性能^[48]

Figure 4 (Color online) Device structure and performance of QLED with mixed hole injection layer^[48]

图5 (网络版彩色) 喷墨打印钙钛矿光电探测器^[57]. (a) 沉积过程示意图; (b) 喷墨打印形成的钙钛矿微米线网络; (c) 电流-电压关系图; (d) 光电探测器阵列和单个像素器件的结构示意图; (e) 能级和工作原理示意图; (f) 输出光电流的空间分布

Figure 5 (Color online) Perovskite-based photodetectors by inkjet printing^[57]. (a) Schematic showing the deposition process; (b) perovskite microwires fabricated by inkjet printing; (c) current characteristics versus voltage of the device; (d) schematic of the photodetector array and the electrode-gap-electrode lateral structure of a single pixel; (e) schematic of energy level and working principle; (f) output photocurrent mapping

用于光电成像传感器, 并成功地映射出清晰光源信号, 如图5(d)~(f). 这项工作有利于实现低成本、高性能的钙钛矿光电传感器.

2.2 钙钛矿光敏突触

得益于神经形态计算, 尤其是人工神经网络的开发, 近年来人工智能蓬勃发展. 然而, 当前的人工智能仍然基于传统的冯·诺依曼计算机, 每次计算都伴随着巨量的能源消耗. 而且, 随着数据量的爆炸增长, 冯·诺依曼计算机已经越来越难以支撑神经形态计算所需的巨大运算能力^[58]. 因此, 构筑全新的计算架构对推动神经形态计算乃至人工智能的发展具有尤为重要的意义. 人脑的神经信息活动具有卓越的特性, 例如大规模并行、分布式存储和处理、自组织、自学习以及低功耗. 生物学研究表明, 人脑的这些出色功能主要得益于神经系统中具有计算和存储功能的生物突触. 基于人工神经突触器件构筑新颖的计算架构来实现神经形态计算被认为是一条极具潜力的道路.

在之前的文献中, 电子突触器件已经被成功提出并以各种方式实施, 其优越的应用潜力已被广泛证实^[58-61]. 对人类而言, 超过80%的外部信息通过视觉感知获得, 因此能够存储并处理视觉信号的光敏突触器件值得深入研究. 然而, 光敏突触器件作为处理视觉信

号最有前途的候选者之一, 其研究仍处于初期阶段^[62,63]. 全无机钙钛矿材料^[64-66]由于其半峰宽窄、光致发光量子产率高、易于调节发光波长以及热稳定性良好而在学术界引起了广泛关注. 鉴于钙钛矿材料具有优异的光敏感特征, 我们将其用于光电神经形态计算领域, 报道了一种基于CsPbBr₃钙钛矿纳米片的双端结构光电突触器件, 如图6(a), 其耦合了光传感和突触可塑性功能, 实现了光电输入信号的智能化处理. 该器件成功地模拟了神经系统的多种突触功能, 如经典的增强/抑制过程(图6(b))、幅度依赖可塑性(图6(c))、成对脉冲促进、短期记忆与长期记忆之间的转换等. 此外, 我们以小规模光电突触阵列演示了独特的“记忆回溯”功能, 如图6(d), 即使经过“遗忘”处理, 该功能也可以挖掘出前期所记忆的信息. 这个功能有助于获取时间维度上的光电信息, 有益于未来光电神经形态计算的开发.

3 总结与展望

与传统电子产品制造方法相比, 溶液加工技术构筑光电子器件在像素图案化、大面积、柔性化、低成本及绿色环保等方面具有无可比拟的优势, 更能满足新一代光电技术发展的要求. 通过溶液法工艺构筑纳米光电材料器件, 需将纳米材料分散在溶剂中形成稳

图6 (网络版彩色)钙钛矿光敏突触^[67]. (a) 光电突触器件结构; (b) 增强/抑制过程; (c) 幅度依赖可塑性; (d) 小规模光电突触阵列上演示的“记忆回溯”功能

Figure 6 (Color online) Perovskite-based optoelectronic synapse^[67]. (a) Optoelectronic synapse device structure; (b) potentiation/depression process; (c) amplitude-dependent plasticity; (d) the “memory backtracking” function demonstrated on a small-scale optoelectronic synapse array

定的溶液(墨水), 通过旋涂、喷墨打印等溶液法工艺制备成薄膜, 随后组装成器件. 墨水作为溶液工艺构筑器件的核心材料, 在未来的电子社会中将会有越来越广泛的应用, 是微电子技术的重要革新基础. 因此, 开发高性能且稳定的纳米光电材料墨水, 研究墨水的输运成膜过程、光电薄膜界面调控、光电器件结构和性能

优化, 不仅具有重大的理论研究意义, 而且还能推动低成本、大面积、柔性光电子技术领域的发展. 此外, 溶液法加工成膜技术源于液体蒸发过程中纳米材料的自组装, 具有传统真空工艺以及外延生长无法实现的成膜多样性, 探索其新型光电应用也是一个有潜力的研究方向.

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Summary for “可溶液加工纳米光电材料与器件”

Solution-processable nano-optoelectronic materials and devices

Yang Liu, Yangbin Zhu, Fumin Ma, Yueting Zheng, Hailong Hu, Tailiang Guo & Fushan Li*

*College of Physics and Information Engineering, Fuzhou University, Fuzhou 350108, China** Corresponding author, E-mail: fsli@fzu.edu.cn

Humans have been seeking low-cost information dissemination and product production methods since ancient times. Nearly two thousand years ago, printing, as one of China's four great inventions, offered great convenience for the systematic accumulation and widespread dissemination of knowledge and information, describing a glorious chapter in the history of human civilization. In the past 50 years, semiconductor silicon materials and its corresponding micro-nano-processing technology have been developed by leaps and bounds, forming an extremely complex technical system. In fact, it now acts an indispensable role in the field of optoelectronics. However, people's increasing demand of smart optoelectronic devices promotes the development of optoelectronic devices towards flexibility and structure miniaturization. As a result, the complexity of traditional semiconductor devices and the limitations of high costs have been becoming more serious, hindering the long-term development of this field. Nano-optoelectronic materials provide a simple solution-processable way to replace the traditional complicated micro-nano-processing techniques. The reason is that they can be stably dispersed in solution through surface modification or exist in the form of liquid precursors, and then be deposited via a solution method to form the required films or patterns. In the past 20 years, nano material has achieved great progress. Nano-photoelectric materials represented by quantum dots and perovskites are characterized with excellent fluorescence quantum yield, high color purity, simple way to tailor spectra by particle size or composition, and convenient solution-processing technique, etc., showing attractive application in the field of optoelectronic devices. The combination of long-standing solution-printing technology and nano-optoelectronic materials is regarded as one of the best candidates which can overcome the complex and costly limitations of traditional semiconductor techniques. It enjoys promising application prospects in low-cost, flexible, patterned and large-area optoelectronic devices.

In this paper, solution processing nano-optoelectronic materials and devices are studied. Nano-photoelectric materials are used to construct devices by solution process. Nano-materials need to be dispersed in a solvent to form a stable solution (so called inks); then, deposited on substrates to form films by solution processes, such as spin coating or inkjet printing, and finally assembled into devices. Inks, as the core material system of the solution-processing technique to construct devices, will achieve more and more extensive optoelectronic applications, and act as an important innovation basis for microelectronics technology in the future. Therefore, it not only has great theoretical significance, but also promotes the development of low-cost large-scale flexible optoelectronic technology to study high-performance and stable nano-photoelectric material inks, ink transportation and film formation process, interface regulation of optoelectronic film, and optimization of device structure and performance.

This paper introduces our systematic progresses in this field in recent years, including preparation of quantum-dot inks, inkjet-printing quantum-dot technology and application, luminescence mechanism of solution-processing quantum-dot interface, and structure design and performance optimization in luminescence, detector, and synaptic device. In addition, the solution-processed film-forming technology relies on the self-assembly of nanomaterials during the liquid evaporation process; that is, it has unique film-forming diversity which cannot be achieved by traditional vacuum technology and epitaxial growth, indicating a potential research direction to explore its new optoelectronic applications, for example, anti-counterfeiting labels. The related researches are of great significance for both academic research and industrial applications.

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