



## 量子点-聚合物纳米复合材料的光电器件研究进展

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### Research advances in optoelectronic devices of quantum dot-polymer nanocomposites

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## 量子点-聚合物纳米复合材料的光电器件研究进展

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**摘要:** 量子点因具有优异的光电特性, 近年来备受关注。但量子点的规模化应用因受到其加工工艺及稳定性等因素限制而尚待开发。量子点-聚合物纳米复合材料的出现有效弥补了这一问题, 将量子点分散到有机聚合物中形成纳米复合材料, 集合量子点与聚合物的各自优势于一体, 是解决量子点当前应用问题的一种有效方法, 具有显著的发展潜力。文中介绍了量子点的主要制备技术, 并在此基础上对量子点-聚合物复合材料的制备方法及其在激光器、发光二极管、光电探测器、量子点电视等光电子器件中的应用进展进行了概述, 最后对其在光电器件领域的应用进行了展望。

**关键词:** 量子点; 聚合物; 纳米复合材料; 制备方法; 光电器件

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## Research advances in optoelectronic devices of quantum dot-polymer nanocomposites

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**Abstract:** Quantum dots have attracted much attention in recent years because of their excellent photoelectric properties. However, the large-scale application of quantum dots has yet to be developed due to its processing technology and stability. The emergence of quantum dot-polymer nanocomposites effectively makes up for this problem. It is an effective method to solve the current application problems of quantum dots by disperses quantum dots into organic polymers to form nanocomposites and integrates the respective advantages of quantum dots and polymers. It has significant development potential. The main preparation technology of quantum dots was introduced, on this basis, the preparation methods of QD-polymer composites and their applications in lasers, light

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emitting diodes, photodetectors, QD-TVs and other optoelectronic devices were summarized, and finally its application in the field of optoelectronic device was prospected.

**Key words:** quantum dots; polymers; nanocomposites; preparation methods; photoelectronic devices

## 0 引言

纳米材料是指在三维空间中至少有一维处于纳米尺度范围的结构(1~100 nm)或是由这种结构作为基本单元构成的材料。纳米材料按照维度可分为二维、一维及零维三种。量子点(Quantum dots, QDs),也称为半导体纳米晶(Nanocrystals, NCs),属于零维纳米材料,通常包含几个到几千个原子,其内部的载流子因受到三个维度的势垒约束不能发生自由运动,当吸收外界的光、热等能量时,价带上的电子跃迁至导带,价带中出现空穴,这些电子和空穴成为自由载流子即可导电。以石墨烯量子点为例,它是由 $sp^2$ 杂化碳原子紧密堆积而形成的蜂窝晶格纳米结构,具有多色发光、高荧光量子产率、激子结合能低、载流子迁移率高、激发光谱较宽等特性,这些优越的光学、电学性能使其成为近年来备受瞩目的量子点材料,并在太阳电池、光电探测器、发光二极管以及激光器等领域显示出巨大的应用潜力,受到越来越多的关注,引发了人们对于零维纳米材料的兴趣,使量子点的相关研究得到迅速发展<sup>[1~3]</sup>。

随着量子点技术的不断成熟,量子点在表现出优越发光性能的同时也存在一些不足,如Cd类半导体量子点具有毒性,导致其应用受到限制<sup>[4]</sup>; InP量子点荧光效率偏低<sup>[5]</sup>; 钙钛矿量子点则易受到温度、光照等因素影响,产生不可逆转的降解,导致荧光猝灭<sup>[6]</sup>。这些问题使量子点的规模化应用受到了限制,因此人们利用不同的技术手段对量子点进行改性,以拓展其应用。以半导体领域中常用的掺杂技术为例:在量子点中引入异原子,可以增大反应活性,提升光子和载流子的特性,增加光致发光强度,使量子点更好地应用于光学器件、光电探测、生物医学等方面<sup>[7~9]</sup>。最近

一系列研究表明:量子点与有机聚合物结合能够有效提升量子点的稳定性及加工性能,有利于获得高效稳定的发光器件,同时有望实现低成本、易工业化生产的要求,应用前景十分广泛<sup>[10~11]</sup>。

## 1 量子点概述

量子点是指空间三个维度上存在量子限域效应的半导体纳米晶材料。1962年,日本物理学家Kubo首次发现了量子尺寸效应,此外,量子点还具有表面效应、量子限域效应以及宏观量子隧道效应等,这些效应使量子点的性质与块体材料存在明显差别。当块体材料尺寸减小到纳米级别时,将会限制载流子的运动,导致动能增大,能隙随之增大,其发光波长范围及发光颜色也随着能隙变化而改变<sup>[12]</sup>,从而导致光吸收带上的谱峰红移(向长波移动)或蓝移(向短波移动),这种可调控的荧光特性在红外探测器、光学遥感大气监测以及激光二极管等光学器件应用领域是非常有利的。

经过长期的发展,量子点的相关研究不断取得突破,各类量子点都实现了成功制备。笔者课题组<sup>[13]</sup>通过液相超声法成功制备了过渡金属碲化物中的CoTe<sub>2</sub>QDs,发现该QDs光致发光强度较强,即使在近红外波段仍存在发光现象,而且荧光量子产率高达62.6%,有望成为新的红外探测器材料。**表1**列出了常见的量子点及其基本特性,其中应用较广泛的是以Cd为代表的Ⅱ-VI族半导体量子点、过渡金属硫族化合物量子点以及近年发展迅猛的钙钛矿量子点<sup>[14]</sup>。目前量子点的制备方法主要有:分子束外延法、电化学法、磁控溅射法、化学气相沉积法、热注入法、液相超声法、溶剂热法和范德瓦尔斯外延生长等<sup>[15~17]</sup>,**图1**所示为其中几种具有代表性的制备方法示意图。

表 1 常见的量子点材料

Tab.1 Common quantum dot materials

Materials	Wavelength/nm	Size/nm	Peak/nm	Photoluminescence quantum yield	Ref.
CdS	/	3.5	505	50%	[18]
CsPbI <sub>3</sub>	/	11-16	673-692	100%	[19]
ZrS <sub>2</sub>	240-360	3	379-454	53.3%	[20]
MA <sub>3</sub> Bi <sub>2</sub> Br <sub>9</sub>	254	3.05	360-540	12%	[21]
MA <sub>3</sub> Bi <sub>2</sub> Cl <sub>9</sub>	254	2-4	360	15%	[21]
CoTe <sub>2</sub>	300-400	3.1	400-448	62.6%	[13]
Sb <sub>2</sub> Te <sub>3</sub>	300-600	2.3	400-450	/	[2]
ReS <sub>2</sub>	320-440	2.7	420-490	75.6%	[22]
N-Ti <sub>3</sub> C <sub>2</sub>	360	3.4	447	18.7%	[23]
ZnSeTe	422-500	5.3	460	75%	[24]
CdTe	480	2.3-2.7	/	80%	[25]
CsPbBr <sub>3</sub>	480	10	/	93%	[26]
WO <sub>3</sub> -WS <sub>2</sub>	600	0.8-2.1	630	11.6%	[27]
CdSe	600-650	4	/	97%	[28]
PbS	785	6-10	700-1 600	26%	[29]
Si	825	4	/	90%	[30]
PbTe	870	5-16	700-1 000	42%	[31]
InP/ZnS	1 200	2.1-4.1	480-590	68%	[5]

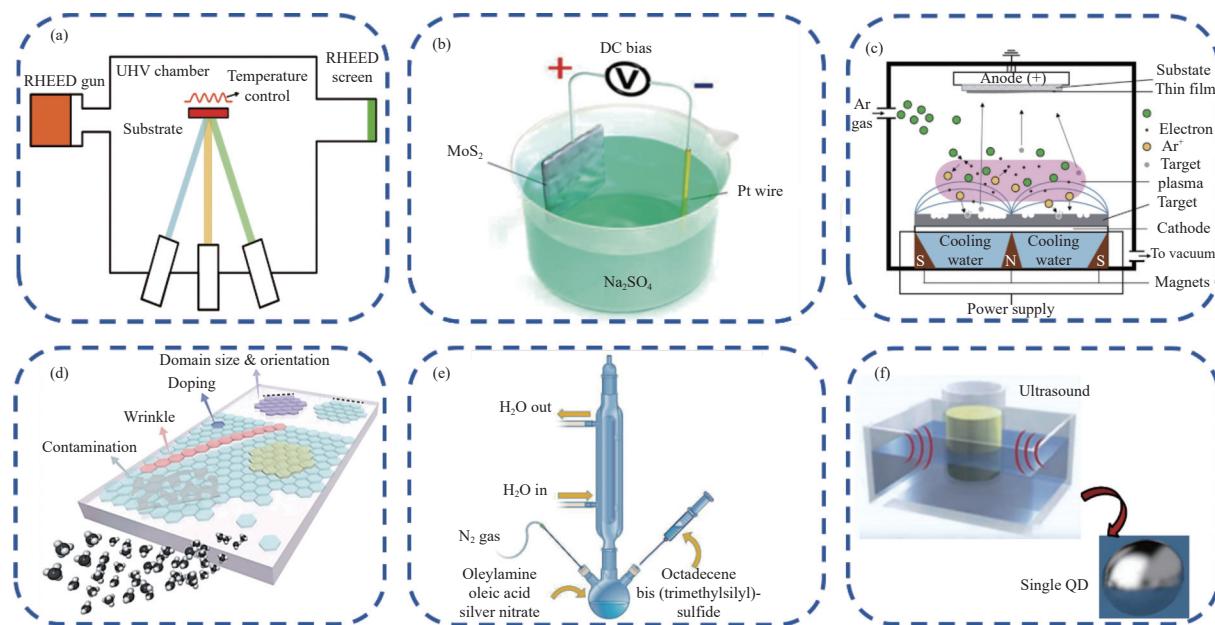


图 1 量子点制备方法示意图: (a) 分子束外延法; (b) 电化学法<sup>[12]</sup>; (c) 磁控溅射法<sup>[32]</sup>; (d) 化学气相沉积法<sup>[33]</sup>; (e) 热注入法<sup>[34]</sup>; (f) 液相超声法<sup>[12]</sup>

Fig.1 Preparation methods of quantum dots: (a) Molecular beam epitaxy; (b) Electrochemical method<sup>[12]</sup>; (c) Magnetron sputtering<sup>[32]</sup>; (d) Chemical vapor deposition<sup>[33]</sup>; (e) Hot injection method<sup>[34]</sup>; (f) Liquid phase ultrasonic method<sup>[12]</sup>

## 2 聚合物概述

有机聚合物普遍具有透光率高、化学稳定性好、易于加工成型等特点。现阶段,实现量子点集成到器件的一种主要方法就是将量子点嵌入聚合物基质中得到杂化或复合的量子点材料,从而提升其性能。因此,聚合物材料的选择对于量子点集成而言尤为重要。

目前,在量子点-聚合物纳米复合材料制备中常

用的聚合物有聚甲基丙烯酸甲酯(PMMA)<sup>[35]</sup>、聚乙烯醇(PVA)<sup>[36]</sup>、聚二甲基硅氧烷(PDMS)、聚乙烯亚胺(PEI)<sup>[37]</sup>、聚四氟乙烯(PTFE)<sup>[38]</sup>和聚苯乙烯(PS)<sup>[39]</sup>等,表 2 列出了部分常见的量子点-聚合物纳米复合材料的相关性能参数。基于聚合物所具有的优良加工性能以及价格低廉、无毒环保、水溶或油溶性等优势,聚合物在荧光太阳能聚光器、量子点电视及红外、紫外探测器等领域都有应用。

表 2 常用的量子点-聚合物纳米复合材料

Tab.2 Commonly used quantum dot-polymer nanocomposites

Materials	Preparation method	Wavelength/nm	Size/nm	Peak/nm	Quantum dot content/wt%	Photoluminescence quantum yield	Ref.
CdTe/PMMA	Thermal evaporation	/	2.21-3.42	538-584	6.1	13.5%	[40]
Si/PMMA	Doctor blading	/	100	750	0-3.3	35%	[41]
PbSe/PVA	Solution casting	200-800	2.1	1110	5	/	[42]
SnO <sub>2</sub> /PCz(Polycarbazole) N-	In-situ chemical polymerization	320-550	15-20	410-422	5-20	/	[43]
CQD/MIPs(Molecularly Imprinted Polymer)	Sol-gel	330	3.2-4.9	431	/	/	[44]
MAPbBr <sub>3</sub> /PMMA	In-situ polymerization	350	4	543	/	88%	[45]
GQD/PVA	Solution casting	350-650	500	/	10	/	[46]
CdSe/PS	Colloidal synthesis	360-370	400-500	510-570	/	/	[47]
CDS/b-PEI(Branched Polyethylenimine)	one-step hydrothermal	365	30-50	508-528	/	90.49%	[48]
CdTe/WPU(Waterborne Polyurethane)	Casting and Evaporating	373	2.5-4.1	528-665	0.3	18%	[49]
TiO <sub>2</sub> /Acrylate	UV polymerization	393	150	530	0.1	/	[50]
InP@GaP/ZnS/PDMS	SAM Encapsulating	400-700	/	527	10	/	[51]
PbSe/PDTPBT(Poly(2,6-(N-(1-octynonyl)dithieno[3,2-b:20,30-d]pyrrole)-alt-4,7-(2,1,3-benzothiadiazole)))	Ligand exchange	400-900	150	700-800	0.9	/	[52]
Sb <sub>2</sub> S <sub>3</sub> /PMMA	One-pot synthesis	450	/	645	9	20%	[35]
CsPbBr <sub>3</sub> /PS	In-situ photoactivated polymerization	450-650	/	530	0.2	44%	[39]
MAPbBr <sub>3</sub> /PDMS	Template	488	5.6-9.8	528	30	10%	[53]
ZnS/MQ(5-(2-methacryloyloxyethyl)-thyl)-8-quinolinol)	In-situ polymerization	495	3	500	/	40%	[54]
WS <sub>2</sub> /PVA	Liquid phase exfoliation	532	60-120	617	/	/	[55]
C/PS	Solvothermal	800	12-35	410-580	0.4	22%	[56]
CeF <sub>3</sub> /PS	Solution casting	975	27-57	1530	10	/	[57]

### 2.1 聚甲基丙烯酸甲酯( PMMA )

聚甲基丙烯酸甲酯(Poly(methyl methacrylate),

PMMA),一种热塑性塑料,不溶于水,透光率高达92%,介电和电绝缘性能良好,韧性和化学稳定性高,

紫外线屏蔽能力强,广泛用于量子点复合材料制备。Huang<sup>[40]</sup>等人采用热蒸发工艺以 PMMA 和水溶性 CdTe QDs 作为原料,制备出具有高光致发光强度的柔性 CdTe/PMMA 复合薄膜,通过配体交换得到油溶性 CdTe QDs,当分别具有 539 nm、555 nm、566 nm 和 588 nm 发射波长的油溶性 CdTe QDs 掺入 PMMA 中后,在波长为 365 nm 的紫外灯照射下,所得的柔性透明复合薄膜分别发出绿色、黄绿色、黄色和橙色荧光。该项研究表明:CdTe QDs 与 PMMA 相容性良好,成膜后的量子点仍保持着良好的荧光性能,且光致发光增强。近年来随着钙钛矿材料研究的快速发展,其优异的光电性能受到人们的广泛关注,但提升稳定性是其亟待解决的问题<sup>[58]</sup>。Zhang 等人<sup>[35]</sup>以 PMMA 和 CsPbBr<sub>3</sub> 为原料,利用紫外光聚合法制备出钙钛矿-聚合物复合材料,研究结果表明 PMMA 有效提升了钙钛矿在空气和水中的稳定性。

## 2.2 聚乙烯醇 (PVA)

聚乙烯醇 (Poly(vinyl alcohol),PVA) 是一种水溶性聚合物,透明度高、热稳定性好、绿色无毒、成膜能力强、化学性能优异。Meng 等人<sup>[59]</sup>采用石墨烯与 PVA 复配并将其拉伸成为纳米纤维,研究结果显示石墨烯自身的结构和机械性能不仅没有受到 PVA 的影响,而且光学非线性得到显著增强,其脉冲能量最低阈值可达 0.25 pJ/pulse。Cosgun 等人<sup>[60]</sup>将掺杂合成得到的 ZnSe:Mn/ZnS QDs 与 PVA 结合,并将复合后的材料用于制作白色荧光 LED,获得具有高发光特性及显色指数值 (CRI) 高达 93.5 的 LED,其在 20 mA 电流下连续工作 25 h 也能保持高稳定性。

## 2.3 聚二甲基硅氧烷 (PDMS)

聚二甲基硅氧烷 (Poly dimethylsiloxane, PDMS) 是由硅、氧连接形成主链组成的热固性材料,属于有机硅化合物,具有光学透明性高、应力低、绿色无毒、耐高低温、吸附性强、与硅衬底相容性好等特性。Song 等人<sup>[61]</sup>设计了一种基于 PDMS 负载的 ZnS 层电致发光器件,此器件通过调制电流频率能够获得可拉伸的特性,而且色彩调节能力得到明显增强。Kim 等人<sup>[62]</sup>基于已有光学触觉传感器的不足设计了一种新

型的石墨烯光波导触觉传感器:利用 PDMS 与石墨烯嵌合调整界面面积,增加石墨烯的吸光量,使上层的折射率大于光波导芯的折射率,实现了实时响应。

## 2.4 聚乙烯亚胺 (PEI)

聚乙烯亚胺 (Polyethyleneimine, PEI) 是一种水溶性聚合物,稳定性极佳,耐热性良好,价格低廉,附着能力强,其丰富的胺基官能团可与量子点产生相互作用进而结合。Li 等人<sup>[63]</sup>利用 PEI 的亲水性处理钙钛矿太阳电池的界面接触,经处理后的电池转换效率 (Power Conversion Efficiency, PCE) 达 14.4%,此外,该电池在自然环境下的稳定性也得到有效改善,10 天内电池效率下降小于 10%。

## 2.5 聚苯乙烯 (PS)

聚苯乙烯 (polystyrene, PS) 是一种强度大、刚性好、化学稳定性高的无毒热塑性聚合物材料。PS 对于量子点在薄膜形成过程中出现的成分流失和相分离现象能起到有效的抑制作用,且具有疏水性的 PS 可以有效隔绝空气中的水分,从而增强量子点的稳定性。Ghimire 等人<sup>[64]</sup>选用壳聚糖-聚苯乙烯共聚物 (Chitosan-Polystryrene, CS-g-PS) 将 CdSe/ZnS QDs 均匀分布在 PS 中,在相转移反应下量子点与聚合物紧密结合,形成 QDs/聚合物共轭膜。研究结果显示:该复合膜能够保护量子点不受外界干扰并保持其强光致发光的特性,且与纯量子点薄膜相比,复合膜的荧光寿命更长,光稳定性更好。

## 3 量子点-聚合物纳米复合材料制备研究现状

随着科技的发展,对多功能材料的需求也日益增长。量子点与聚合物结合实现性能互补的关键在于保持量子点的分散性,只有充分地均匀分散,量子点与聚合物的嵌合才能发挥出复合材料的最大优势<sup>[65]</sup>。但实际应用中量子点容易聚集,因此复合材料的制备方法就显得尤为重要。该节综述了溶胶-凝胶法、微乳液法、原位聚合法及其混合法等几种常见的制备量子点纳米复合材料的方法,图 2 列出了上述制备方法的原理示意图。

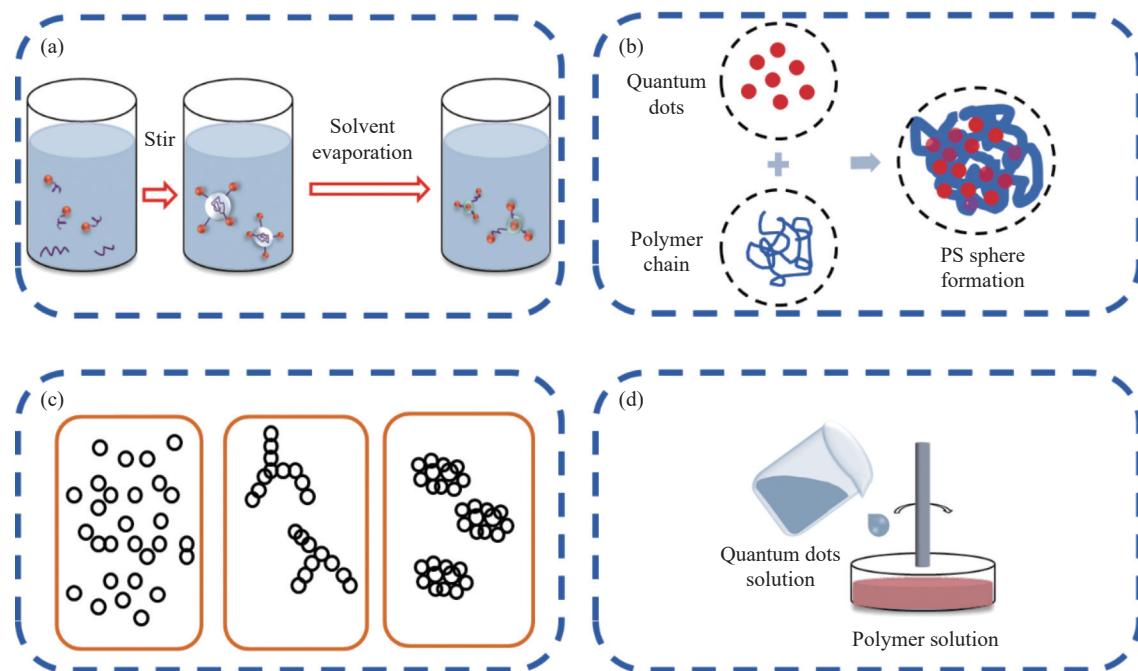


图 2 复合材料制备方法示意图: (a) 微乳液法; (b) 原位聚合法; (c) 溶胶-凝胶法; (d) 共混法

Fig.2 Schematic diagram of composite preparation methods: (a) Microemulsion method; (b) In-situ polymerization method; (c) Sol-gel method; (d) Blending method

### 3.1 溶胶-凝胶法

溶胶-凝胶法<sup>[66]</sup>适用于易水解化合物制备纳米材料,量子点在胶状的基质中沉淀可以改善其晶体结构缺陷。为了确保反应的顺利进行,需要选择水溶性的化合物进行水解和缩合反应形成纳米晶体,经过聚集陈化以后形成凝胶状,经烘干等处理便可得到量子点纳米复合材料。溶胶-凝胶法可以调控溶液的 pH 值和浓度,有效控制纳米晶体的生长速度,制备出分布均匀的量子点复合薄膜。由于 CdS QDs 能够在胶体基质中生成,且尺寸均匀,并产生高的光增益效果,因此许多含镉类化合物的无机-有机复合材料都是采用溶胶-凝胶法制备的。Zhang 等人<sup>[67]</sup>利用溶胶-凝胶法制作了一种基于分子印迹聚合物 (Molecularly Imprinted Polymer, MIP) 包覆的 CdTe QDs 蛋白质识别传感器,该传感器不仅具有量子点的荧光特性,还有分子印迹技术的高选择性,成功地将特异性作用转化为荧光信号。目前该类分子印迹技术已广泛应用于纳米传感器的制备。

### 3.2 微乳液法

微乳液法<sup>[68]</sup>也称为反胶束法,利用相似相溶的原理,借助表面活性剂产生纳米级的溶剂粒子,形成

稳定的微乳液,合成的整个过程都是在微小的球形液滴中进行的。该法适用于多种金属及其化合物的制备。1980 年, Stoffer 团队<sup>[69]</sup>第一次在微乳液法中引入有机高分子材料,由此得到了微乳液聚合技术。在微乳液法中,纳米材料的生长被限制在胶束内部,其尺寸主要依赖于胶束的大小,因此借助此方法可以控制纳米材料的尺寸和粒度分布。Chen 等人<sup>[70]</sup>利用微乳液法制备得到半导体聚合物量子点,该法能够降低半导体量子点的毒性,使其用于生物成像。但微乳液法会影响量子点的荧光强度和量子产率。甘礼华等人<sup>[71]</sup>将反相乳液法和溶胶-凝胶法相结合制备了钛硅氧化物多孔微球,得到的球体平均尺寸为 100 μm,平均孔径 15 nm,研究结果表明:该微球具有良好的光催化活性,在污水降解领域有良好的应用潜力。Harun 等人<sup>[72]</sup>借助细乳液法将 Si QDs 和 Ag NCs 封装在聚二乙烯基苯中,合成了具有发光特性的可加工复合材料,该复合材料平均粒径在 110~120 nm 之间,其发光强度比未进行复合的 Si QDs 更强,用该材料进行喷墨打印,可在玻璃基板上形成均匀规则的圆斑,表明该材料可应用于喷墨打印技术。

### 3.3 原位聚合法

原位聚合法是先将纳米粒子在单体中均匀分散,然后利用引发剂引发聚合反应,使纳米粒子或分子均匀地分散在聚合物基体中形成原位分子聚合材料<sup>[73]</sup>。原位聚合过程中发生的强烈化学反应对配体结合的影响非常大,需要在溶剂的辅助下进行量子点与聚合物的复合,使量子点保持原有特性。Mecking 等人<sup>[74]</sup>利用原位聚合法将聚乙烯(Polyethylene, PE)与石墨烯进行复合,经研究对比,这种复合材料与未复合的石墨烯相比,渗透阈值明显降低,约为 2 wt%。Park 等人<sup>[75]</sup>利用原位聚合法制备 InP QDs/ODE(1-octadecene)复合材料,InP QDs 被聚合物有效钝化,稳定性显著提升。将该复合材料用于白光 LED,测得外部量子效率为 160 lm/W,有效提升了器件的性能。

### 3.4 共混法

共混法是通过物理机械作用直接将纳米颗粒与聚合物混合得到复合材料的方法。按照聚合物的性质该方法可分为两类:溶液共混和熔融共混。溶液共混也称溶液浇铸法,将量子点与液态聚合物溶剂混合,通过物理方法使其均匀分散。熔融共混是通过混合搅拌使量子点分散在熔融状态的聚合物中。Mallakpour 等人<sup>[76]</sup>将聚乙二醇掺入乙醇溶液中,再与完成表面改性的 Al<sub>2</sub>O<sub>3</sub> 纳米颗粒进行溶液共混,得到在紫外区域

有良好光吸收性能的透明纳米复合薄膜,可用作屏蔽紫外线的涂层。Lin 等人<sup>[77]</sup>使用原位聚合法制备出 PE,然后通过共混法将 PE 接枝在石墨烯表面,得到了石墨烯/PE 复合材料,极大提高了量子点的分散性及与聚合物的相容性,机械性能也得到明显改善。Kovalchuk 等人<sup>[46]</sup>利用溶液共混法制备了石墨烯量子点(Graphene Quantum Dots, GQD)-PVA 复合发光材料,研究了不同量子点浓度下材料的光学、热学及荧光性质,结论如下:GQD 浓度为 1~5 wt% 时,材料的光学透明度高达 78%~91%,且此时量子点分散性最佳;当 GQD 浓度在 10 wt% 以下时,材料的光致发光强度随浓度增加而增加,具有浓度依赖性,当浓度等于 10 wt% 时,光致发光强度达到最大值,以上研究结果表明 GQD-PVA 复合材料的特性与量子点浓度有关。

## 4 量子点-聚合物纳米复合材料在光电器件的应用概述

量子点在光电领域的应用一直备受关注,量子点通过与聚合物结合改善了自身的团聚现象,填补了量子点之间的空隙<sup>[78]</sup>,进一步提升了材料的光学性能,拓宽了其应用范围,有效促进了高性能、低成本的光电器件发展。如图 3 所示,近年来基于量子点-聚合物纳米复合材料的光电器件发展迅速,从早期的照

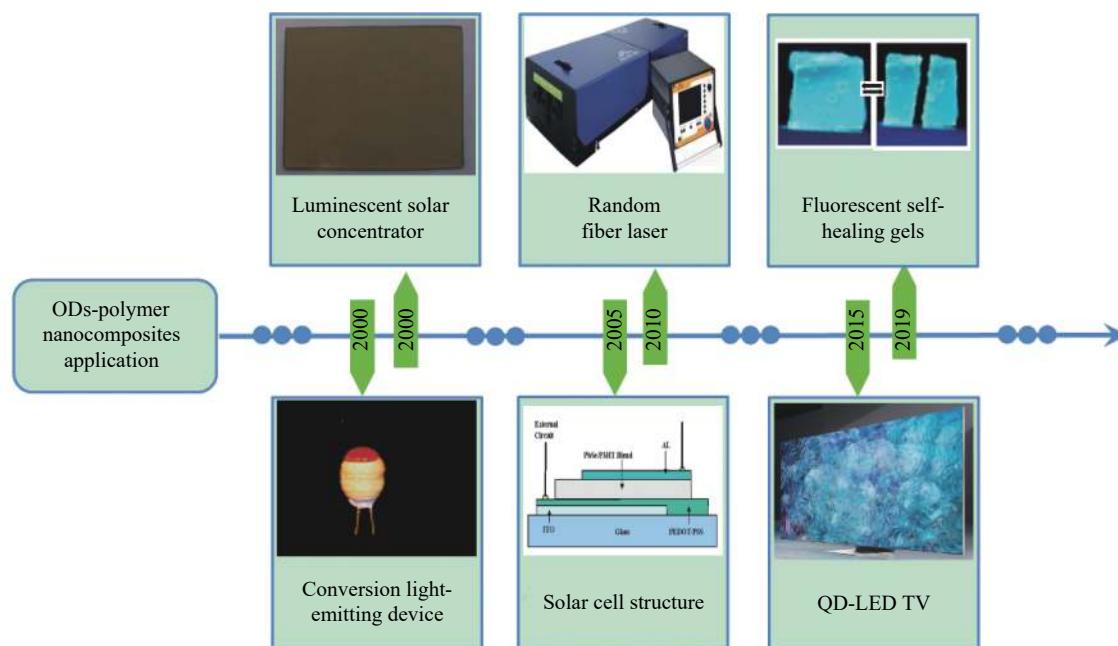


图 3 基于量子点-聚合物纳米复合材料的器件发展进程

Fig.3 Device development process based on quantum dot-polymer nanocomposites

明、太阳能利用,到现阶段的激光、显示等领域都能看到复合材料的身影<sup>[79–80]</sup>。

#### 4.1 激光器

激光器是 20 世纪的重大发明之一,如今科技的进步让激光器也步入了纳米时代<sup>[81]</sup>,朝着器件体积小型化,性能放大的方向发展。Revilla 等人<sup>[82]</sup>发现掺杂硅胶的  $\text{SiO}_2$  QDs 光子泵浦随机激光器产生的激光束穿透深度更大,荧光光子传播距离也更长。Wang 等人<sup>[83]</sup>利用碳量子点(CQD)与 PMMA 形成的复合

材料制备出具有耳语画廊模式(Whispering-Gallery-Mode, WGM)的新型微气泡激光器,研究结果显示该激光器的激光发射波长随着量子点尺寸的变化而改变,且稳定性好,表明 CQD/PMMA 复合材料具有在激光器领域应用的潜力。Wan 等人<sup>[84]</sup>基于喷墨打印技术制作了 CQDs 微激光器,并在 CQD 中掺杂了不同重量占比的 PS,结果表明:当 PS 浓度为 1 wt% 时,激光器的光谱纯度显著提高,且发射波长出现了约 25 nm 的蓝移,其制备示意图如图 4(a) 所示。

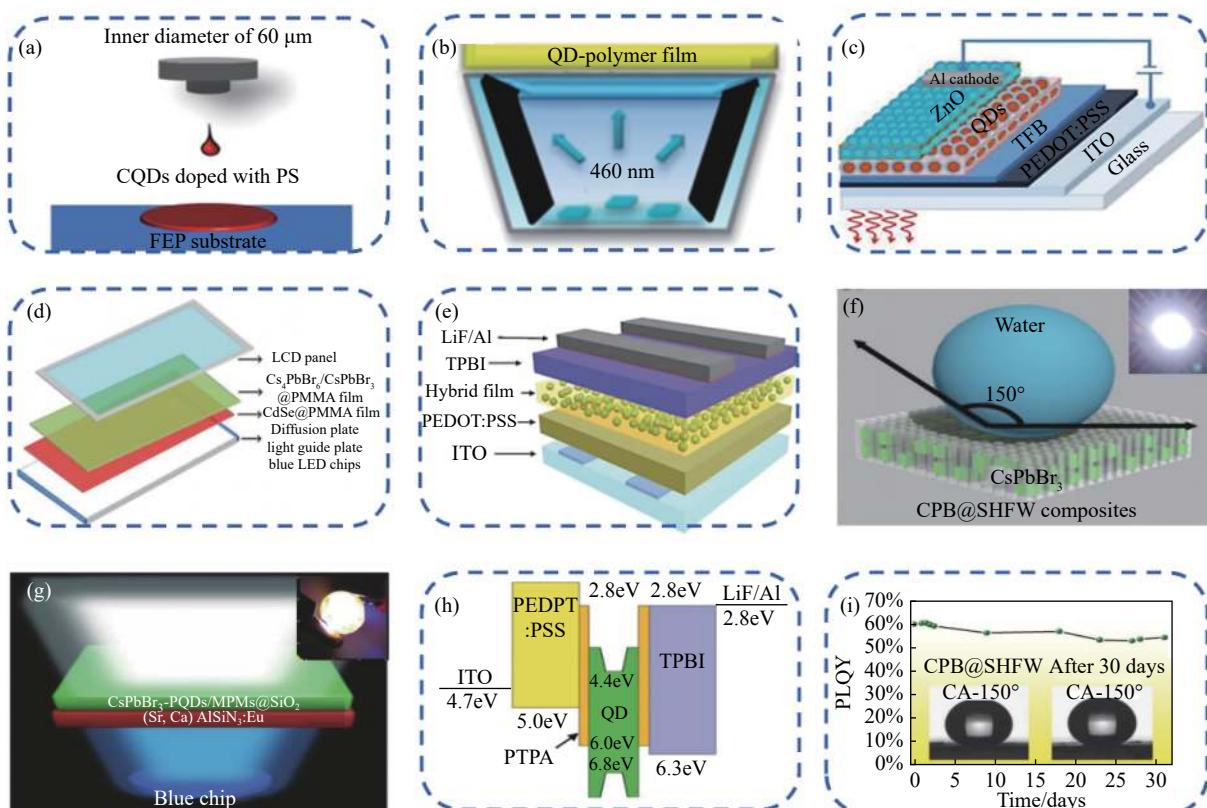


图 4 (a) 基于喷墨打印技术制作 CQDs 微激光器的方案<sup>[84]</sup>; (b) QD-WLED 结构示意图<sup>[85]</sup>; (c) ZnO 发光二极管器件结构示意图<sup>[86]</sup>; (d) 使用蓝色 LED 芯片组合的背光单元装置结构<sup>[87]</sup>; (e) QD/PTPA-b-CAA 制备的 QLED 器件结构示意图<sup>[88]</sup>; (f) CPB@SHFW 复合材料结构示意图,右上角插图为 LED<sup>[89]</sup>; (g)  $\text{CsPbBr}_3$ -P QDs 与介孔聚苯乙烯(MPMs)在  $\text{SiO}_2$  包覆下制备的杂化微球制备的白光 LED 结构图,插图是 LED 在 10 mA 时拍摄的照片<sup>[26]</sup>; (h) QD/PTPA-b-CAA 制备的 QLED 混合发射层能带结构图<sup>[88]</sup>; (i) 浸泡在水中的 CPB@SHFW 复合粉末其 PLQY 随时间的变化图(插图:材料在水中浸泡 31 天)<sup>[89]</sup>

Fig.4 (a) Schematic of fabricating CQDs microlaser based on the inkjet printing technique<sup>[84]</sup>; (b) QD-WLED structure diagram<sup>[85]</sup>; (c) ZnO light-emitting diode device structure diagram<sup>[86]</sup>; (d) Device structure with a combined backlight unit using a blue LED chip<sup>[87]</sup>; (e) Structure diagram of QLED device prepared by QD/ PTPA-B-CAA<sup>[88]</sup>; (f) CPB@SHFW composites structural diagram, upper right illustration is LED<sup>[89]</sup>; (g) Structure diagram of white LED prepared by hybrid microspheres of  $\text{CsPbBr}_3$ -P QDs and mesoporous polystyrene (MPMs) coated with  $\text{SiO}_2$ , the inset is a digital photo of the device taken at 10 mA<sup>[26]</sup>; (h) Energy band structure diagram of QLED hybrid emitting layer prepared by QD/ PTPA-B-CAA<sup>[88]</sup>; (i) Variation of PLQY of CPB@SHFW composite powder with time in water (illustration: material soaked in water for 31 days)<sup>[89]</sup>

## 4.2 发光二极管

发光二极管因具有响应时间快、制造成本低等优点被广泛用于量子点显示板、背光模组等显示领域<sup>[90-91]</sup>。与传统的发光二极管相比,量子点发光二极管(Quantum Dots Light Emitting Diodes, QLED)结构简单、色域宽、功耗低、寿命长,是目前显示设备的主流选择。发光二极管主要由导电层和发光层组成<sup>[92]</sup>,量子点-聚合物复合薄膜是制作发光层的主要材料,负责电子运输。当量子点具有两种或两种以上的发光颜色时,被光源激发后能够产生高亮度的宽色域(>100%NTSC 1931)。但复合薄膜在粒子间的相互作用下通常会发生 Förster(福斯特)共振能量转移(FRET),导致光致发光红移,进而使发光颜色变化。Chen 等人<sup>[85]</sup>提出了一种简便的复合薄膜制备方法以消除福斯特效应,避免复合膜发生红移,并利用该法制备的复合膜制作了白色量子点发光二极管,其结构如图 4(b) 所示。Acharya 等人<sup>[86]</sup>选用一种酸性树脂对 ZnO QDs 进行封装并制备了 QLED,该 QLED 的性能最初是下降的,但随着时间的增加性能会逐渐提升,他们将这种积极的衰老反应称为“正老化”。此外,结果还表明:该复合 QLED 对三原色都有着大于 12% 的外部量子效率,并且在亮度为 2550 尼特时使用寿命长达 470 h,有望用于显视和照明等器件并提供更长的使用寿命,其结构组成如图 4(c) 所示。Li 等人<sup>[87]</sup>将通过原位制备的 Cs<sub>4</sub>PbBr<sub>6</sub>/CsPbBr<sub>3</sub> 量子点复合材料溶于 PMMA 溶液形成了双层保护膜,既能避免 CsPbBr<sub>3</sub> 发生氧化,又能使其保持足够的光稳定性和水稳定性。将该复合材料用于背光液晶显示器后,测得显示器色域为 131% NTSC 和 98% Rec.2020,颜色纯度得到明显提升,其装置结构如图 4(d) 所示。Kwak 等人<sup>[88]</sup>制备了 CdSe@ZnS QD/PTPA-b-CAA(Poly(*p*-methyltriphenylamine-*b*-cysteamine acrylamide)杂化薄膜,结构如图 4(e) 所示,并用该薄膜制作了 QLED,其混合发射层的能带结构如图 4(h) 所示,通过电致发光测得该 QLED 的外量子效率大于 1.5%。Xuan 等人<sup>[89]</sup>将 CsPbBr<sub>3</sub> QDs 嵌入超疏水多孔有机聚合物框架(Super-hydrophobic porous organic polymer frameworks, SHFW)内形成复合材料,其结构如图 4(f) 所示,因聚合物有效提升了 CsPbBr<sub>3</sub> QDs 的稳定性,如图 4(i) 所

示:CsPbBr<sub>3</sub> QDs 即使长时间浸泡在水中也能保持较高的荧光量子产率。利用该复合材料制备的白色 QLED 的发光效率为 50 lm/W, 色域为 127% NTSC。Yang 等人<sup>[26]</sup>将 CsPbBr<sub>3</sub> QDs 嵌入介孔聚苯乙烯微球(mesoporous polystyrene microspheres, MPMs)中并用 SiO<sub>2</sub> 覆盖在微球表面形成 CsPbBr<sub>3</sub> QDs/MPMs@SiO<sub>2</sub> 杂化微球,其荧光量子产率高达 84%,在水中浸泡 30 天后荧光强度为初始值的 48%,用该杂化微球制备的 LED 光度效率高达 81 lm/W,即使长时间工作也能保持良好的稳定性,图 4(g) 为该 LED 的结构示意图。

## 4.3 光电探测器

光电探测器是一种利用半导体材料的光电效应将光信号转换为电信号的光电器件,纳米技术的发展促使光电探测器产生了巨大的变化。以量子点光电探测器为例,其具有灵敏度高、光致发光强度大、稳定性好等特性,且成本比传统的半导体光电探测器更低。根据光电探测器对不同光谱区域的响应特性可以将其应用到相应的领域<sup>[93]</sup>。如紫外-可见光电探测器可用于天文探测、森林防火、电力设备检测等;可见光和近红外光电探测器可用于智能手机、数码相机、遥感器等;多波段中红外光电探测器可用于医疗诊断、生物成像、助航等。图 5(a)~5(d) 是几种新型纳米光电探测器的原理或结构图。Chen 等人<sup>[94]</sup>合成了 CdTe/P3 HT(poly(3-hexylthiophene)) 薄膜层,并加入 PMDTC (N-phenyl-N'-methyldithiocarbamate) 以增加 CdTe 纳米粒子的溶解度,即便在浓度高达 30% (300 mg/ml) 的二氯苯溶液中 CdTe 纳米粒子也没有出现聚集现象。采用该薄膜材料制成的探测器结构如图 5(e) 所示,该探测器在小于 -5 V 的低电压下获得了当时纳米聚合物体系中最高的光导增益,其 J-V 曲线如图 5(h) 所示。Guo 等人<sup>[95]</sup>通过将聚合物 P3 HT、PVK (polyvinylcarbazole) 与 ZnO 纳米粒子复合,制备出一种具有高响应度的紫外光电探测器,其结构组成和工作原理分别如图 5(f)、5(i) 所示。Wei 等人<sup>[96]</sup>利用聚合物 P3 HT 对 CdTe 量子点进行选择性钝化从而提升光电探测器的响应速度,结果表明:(P3 HT):CdTe QDs 光电探测器能继续保持高增益,且响应时间更短,有望实现紫外-可见波长范围内的弱光探测,其器件结构如图 5(g) 所示。

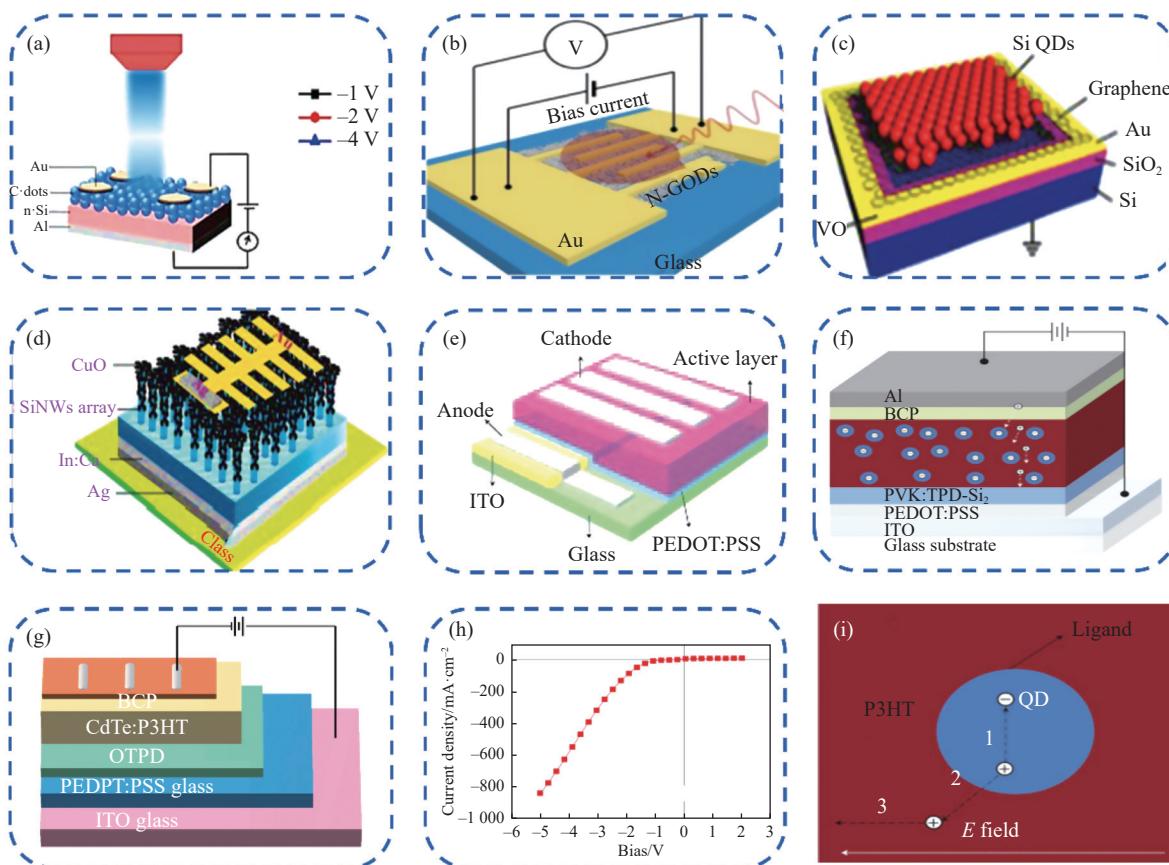


图 5 光电探测器: (a) Au/CNDs/n-Si 紫外光电探测器的装置<sup>[93]</sup>; (b) N-GQDs 光电探测器原理图<sup>[93]</sup>; (c) 典型的 Si-QD/石墨烯/Si 光电探测器<sup>[93]</sup>; (d) Si NWs 阵列/CuO 异质结构光电探测器<sup>[93]</sup>; (e) PMDTC 配体的器件结构<sup>[94]</sup>; (f) ZnO/P3 HT:PVK 光电探测器结构示意图, BCP 层为量子点和聚合物复合层<sup>[95]</sup>; (g) CdTe 和 P3 HT 光电探测器结构<sup>[96]</sup>; (h) 器件在光照射下的 J-V 曲线。在反向偏压下观察到更高的光电流密度<sup>[94]</sup>; (i) 量子点-聚合物复合材料中电子-空穴对的 1 产生、2 分裂、3 空穴传输和电子捕获过程的说明<sup>[95]</sup>

Fig.5 Photoelectric detector: (a) Device of Au/CNDs/n-Si ultraviolet photoelectric detector<sup>[93]</sup>; (b) N-GQDs photodetector schematic diagram<sup>[93]</sup>; (c) Typical Si-QD/Graphene /Si photodetector<sup>[93]</sup>; (d) Si NWs array /CuO heterostructure photodetector<sup>[93]</sup>; (e) Device structure of the PMDTC ligand<sup>[94]</sup>; (f) Schematic diagram of ZnO/P3 HT:PVK photodetector structure, the BCP layer is a composite layer of Quantum dots and polymer<sup>[95]</sup>; (g) CdTe and P3 HT photodetector structure<sup>[96]</sup>; (h) J-V curve of the device under light irradiation. Higher photocurrent density was observed under reverse bias<sup>[94]</sup>; (i) Description of 1 the generation, 2 splitting, 3 hole transport, and electron capture processes of electron-hole pairs in quantum dot polymer composites<sup>[95]</sup>

#### 4.4 量子点电视

随着人们对显示设备的色彩及实用性要求的不断提升,现代显示器件正向着高分辨率、高亮度、彩色化、节能化及大屏幕的方向发展。量子点显示技术(QLED)因具有色域高、亮度高、寿命长、性价比高、能耗比低等优势,近年来已经成为中高端电视显示技术的主流。量子点在电视显示中的应用形式主要有芯片封装型、侧管封装型和量子点膜型三种。其中,量子点膜型一般由量子点和 PMMA 类聚合物组成,封装在阻隔层中制成光学膜,没有和光源直接接

触,相比其他两种类型其性质更稳定,极大减少了量子点发生荧光淬灭的现象,因此实际应用中普遍采用该形式。2015 年,三星率先推出了基于量子点膜型的 CdSe 量子点电视<sup>[97]</sup>,尽管含 Cd 材料具有毒性,但其高发光效率却很难被替代。由此可见,开发绿色新型量子点已成为显示领域亟待解决的难题。2020 年,三星 Eunjoo Jang 团队<sup>[4]</sup>成功研制出一种量子产率为 100% 的无镉蓝光 ZnTeSe / ZnSe / ZnS 量子点,实现了蓝色 QLED 技术的突破,器件的外量子效率高达 20.2%,亮度也显著提高,为 88 900 cd/m<sup>2</sup>,有望引领绿

色量子显示技术新革命,促进量子点电视的商业化发展。

## 5 结论及展望

近年来,量子点-聚合物纳米复合材料的制备研究取得了迅猛发展,复合材料的发光性能也不断提升,在照明、显示、太阳电池、光电器件等领域都有优异的表现,显现出巨大的商业价值,发展前景光明。

尽管量子点-聚合物纳米复合材料在光电领域的应用成果受到广泛关注,但随着发光器件性能的不断提升,对复合材料的要求也随之提高,既要具备高效、稳定的发光特性,还要满足成本低、易规模化生产的要求。鉴于此,今后量子点-聚合物纳米复合材料需要重点解决以下几个方面的问题:(1)新型量子点的制备研究。开发光学性能优异、稳定性好、成本低廉、绿色环保、可量产的量子点是实现其规模化应用的前提;(2)量子点与聚合物的匹配性研究。根据量子点的特性选择合适的聚合物及复合材料的制备方法,促使量子点与聚合物产生协同效应是实现其规模化应用的关键;(3)量子点-聚合物纳米复合材料性能调控研究。通过对量子点性能的调控达到复合材料性能可调的目标,使其发光特性满足不同的应用需求,从而拓展量子点-聚合物纳米复合材料的应用空间。

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