

引用格式: WANG Chenhui, CAI Junhu, HU Xinpei, et al. Research on the Properties of CsPbBr₃ Quantum Dots Modified by Ion Exchange Resin[J]. Acta Photonica Sinica, 2022, 51(6):0616001

王晨辉,蔡俊虎,胡新培,等. 离子交换树脂改性的CsPbBr₃量子点特性研究[J]. 光子学报, 2022, 51(6):0616001

离子交换树脂改性的CsPbBr₃量子点特性研究

王晨辉¹, 蔡俊虎¹, 胡新培¹, 陈恩果^{1,2}, 徐胜^{1,2}, 叶芸^{1,2}, 郭太良^{1,2}

(1 福州大学 物理与信息工程学院, 福州 350108)

(2 中国福建光电信息科学与技术创新实验室(闽都创新实验室), 福州 350108)

摘 要:全无机钙钛矿量子点(PQDs)对环境的不稳定性问题成为了制约其实际应用的潜在威胁,从PQDs材料本身出发研究相应的性能和稳定性提升方案意义重大。本文通过引入离子交换树脂的缺陷钝化和选择性去除作用,实现了同时对CsPbBr₃ PQDs性能改善和稳定性提升。一方面,引入离子交换树脂可以在不改变PQDs固有晶相的情况下选择性地去除形貌差、结构不稳定的PQDs单晶,这使得所制备的PQDs的表面形貌和均一性得到了很大程度的改善,并且在长时间紫外光照和高温实验下,PQDs的稳定性也得到较大提升;另一方面,在改性前后,CsPbBr₃ PQDs的光致发光量子产率(PLQY)和荧光寿命都有了显著提升,PLQY从53.23%提高到了90.00%,荧光寿命则从10.4 ns提高到了22.2 ns。本文研究为PQDs的性能改善与稳定性提升提供了新的思路,由于离子交换树脂可再生和低成本的特性,在光电领域具有广阔的应用前景。

关键词:钙钛矿量子点;离子交换树脂;缺陷钝化;选择性吸附;性能提升

中图分类号:O482.31

文献标识码:A

doi:10.3788/gzxb20225106.0616001

0 引言

全无机钙钛矿量子点(Perovskite Quantum Dots, PQDs)因具有高吸收能力、较窄的发射光谱半峰宽(Full Width at Half Maximum, FWHM)、高光致发光量子产率(Photoluminescence Quantum Yield, PLQY)、组分和尺寸可控、发射光谱可调等优点,目前正成为最有应用前景的光电材料之一^[1-6],其应用已经覆盖了大部分光电领域,包括发光二极管、太阳能电池、光电探测器、激光器等^[7-11]。全无机卤化铅PQDs(CsPbX₃, X=Cl, Br, I)不仅具有与传统全无机II-VI和III-V族量子点相当的优良品质^[12],而且与有机-无机杂化PQDs相比,对氧和水的敏感性更低^[13, 14],但仍然无法达到实际应用的水准,因此需要对其各项性能尤其是稳定性进行改善。

近年来,研究者们主要通过对PQDs表面或其周围进行有机和无机改性来提高PQDs的稳定性。在无机改性方法中,为了提高PQDs的环境稳定性,通常采用二氧化硅(SiO₂)包覆法^[15-17]。此外,还有采用其他无机材料如ZnS、TiO₂和SiO₂/Al₂O₃等来提高PQDs的稳定性^[18]。在有机改性路线中,配体包覆是一种非常简单的提高PQDs稳定性的方法,但由于有机配体较易脱落,所以这种方法很难提供长期的保护^[19]。无论是无机改性还是有机改性,大多是将PQDs封装在疏水材料中,为其提供一个抵御环境变化的物理屏障,而材料本身的缺陷及性能不稳定等问题并未得到有效改善。因此,从钙钛矿材料本身出发研究相应的改性方案十分必要。

离子交换树脂是带有官能团(有交换离子的活性基团)、具有网状结构、不溶性的高分子化合物。对阴离子交换树脂来说,其活性基团可吸附不同类型的阴离子以实现离子交换反应,而PQDs是一类离子化合物

基金项目:国家自然科学基金(No. 62175032),福建省自然科学基金(No. 2021J01579),福建省科技重大专项(No. 2021HZ021001),闽都创新实验室自主部署项目(No. 2020ZZ111)

第一作者:王晨辉(1997—),男,硕士研究生,主要研究方向为量子点发光材料与器件。Email: 502658760@qq.com

导师(通讯作者):陈恩果(1984—),男,副教授,博士,主要研究方向为先进显示技术。Email: ceg@fzu.edu.cn

收稿日期:2022-01-04; **录用日期:**2022-03-18

<http://www.photon.ac.cn>

并含有卤素阴离子,两者具有较好的可结合性。本文基于高温热注入法制备 CsPbBr₃ PQDs,再通过引入阴离子交换树脂,发现了在不改变 PQDs 固有晶相的情况下,能够选择性地去除形貌差、结构不稳定的 PQDs 单晶,通过进一步测试分析发现,该方法制备的 PQDs 在形貌、性能和荧光寿命方面都有了不同程度的改善。

1 实验

1.1 CsPbBr₃ PQDs 的制备

首先制备油酸铯前驱体,取 0.4 g Cs₂CO₃ 与 1.5 mL 油酸、20 mL 十八烯混合在三颈烧瓶中通入氮气形成惰性气体氛围后,加热至 120 °C 并持续搅拌 1 h,之后升温至 160 °C,继续搅拌 20 min 获得油酸铯前驱体溶液,前驱体溶液在使用之前预先加热至 120 °C。之后取 0.15 g PbBr₂ 与 25 mL 十八烯混合在三颈烧瓶中通入氮气搅拌 30 mL,然后升温至 120 °C 继续搅拌 30 min,此时将 1 mL 油酸与 2 mL 油胺混合在药品瓶中并快速注射进反应瓶中,搅拌 10 s 后得到清澈溶液,之后迅速升温至 180 °C,快速注入 2 mL 油酸铯的前驱体溶液,反应 3 s 后立即转移至冰水中使其降温,待溶液温度降到 30 °C 以下后进行提纯处理。将产物置于离心机中以 10 000 r/min 离心 8 min,离心后取沉淀分散在环己烷中,利用超声使沉淀完全分散,再以 5 000 r/min 离心 8 min,离心后取上清液保存。

1.2 阴离子交换树脂的类型转换

阴离子交换树脂的原出厂类型为氢氧型,使用前需将其转换为 Br 型,步骤为:取 10 g 去离子水置于药品瓶中并加入 9.05 g NaBr,放入磁石并以 500 r/min 搅拌 5 min 使 NaBr 完全溶解制成饱和 NaBr 溶液。取 1 g 的阴离子交换树脂加入 NaBr 饱和溶液中,继续搅拌 6 h 后通过过滤取出阴离子交换树脂,再一次重复上述步骤将树脂转化为 Br 型,将过滤后的阴离子交换树脂置于 60 °C 的干燥箱中 1 h 使其完全干燥,最后存放在药品瓶中以备使用。

1.3 CsPbBr₃ PQDs 的改性

将干燥后的 Br 型阴离子交换树脂与 CsPbBr₃ PQDs 溶液按照 1 g/20 ml 的比例进行混合,并在 500 r/min 下持续搅拌 2 h,达到预定的反应时间后通过过滤将溶液部分取出。将反应完成的 PQDs 溶液置于离心管中,以 5 000 r/min 离心 8 min 后取上清液保存。

1.4 样品的表征

使用扫描电子显微镜(Scanning Electron Microscope, SEM)观察阴离子交换树脂的表面形貌,使用透射电子显微镜(Transmission Electron Microscope, TEM)观察 PQDs 的晶体形貌。使用荧光分光光度计测试 PQDs 的光致发光(Photoluminescence, PL)光谱,使用荧光寿命测试系统测试 PQDs 的时间分辨光致发光(Time Resolution Photoluminescence, TRPL)光谱,使用稳态瞬态荧光光谱分析仪测试 PQDs 的 PLQY。使用鼓风干燥箱模拟高温环境,使用紫外分析仪模拟紫外光照环境。上述提及实验仪器的型号等信息汇总在表 1 中。

表 1 实验仪器的型号与生产厂商

Table 1 Model and manufacturer of experimental instruments

Instrument	Model	Manufacturer
SEM	TESCAN MIRA LMS	Tescan
TEM	TECNAI G2 F20	FEI Company
Fluorescence Spectrophotometer	F-4600	SHIMADZU
Fluorescence Lifetime Testing System	Tempo-01	SHIMADZU
Steady State Transient Fluorescence Spectrometer	FLS-980	Edinburgh Instruments
Blast Drying Oven	DHG-9055A	Shanghai Huitai
Ultraviolet Analyzer	ZF1-II	Shanghai Jiapeng

2 实验过程分析

2.1 样品的制备分析

为了方便对比,本文使用了最常见的高温热注入法合成了 CsPbBr₃ PQDs,将热注射时的温度严格控制

在 $180 \pm 2^\circ\text{C}$ 以得到立方相的钙钛矿晶体,同时该温度不超过油酸的沸点 195°C ,避免了因配体减少导致的缺陷增多和性能变差。除油酸外还选用油胺作为量子点表面的配体,配体的引入是为了尽可能的降低量子点表面的缺陷态,这些有机配体在极性较强的溶剂环境下更容易脱落导致量子点的团聚和猝灭^[20, 21],因此选用弱极性的环己烷作为溶剂。油酸铯前驱体在制备和保存时应注意严格隔绝空气,因为油酸铯容易被氧化,这会使合成的量子点质量下降,可以通过直接观察溶液颜色判断前驱体是否被氧化,如图1所示,正常未被氧化的前驱体溶液在室温下呈现出白色沉淀和无色上清液,被氧化后上清液则呈现黄褐色。注射前驱体溶液后的反应时间一般不宜过长,反应时间过长会导致生成的PQDs粒径偏大且分布不均,这是因为前驱体反应活性高时大量晶种的快速成核导致最终尺寸较小的晶粒。相反,前驱体活性低时将导致最终尺寸较大的晶粒^[22]。

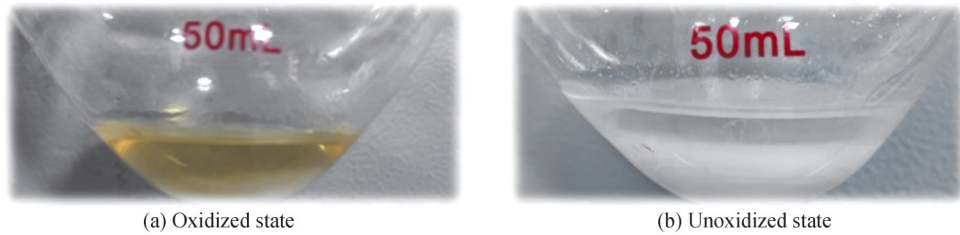


图1 油酸铯前驱体溶液
Fig.1 Cesium oleate precursor solution

2.2 阴离子交换树脂的类型转换分析

实验中使用的树脂为大孔型强碱性阴离子交换树脂,该树脂的惰性高分子网络骨架由苯乙烯与二乙烯苯共聚形成,交换基团为季铵基($-\text{N}(\text{CH}_3)_3$),外观为淡黄至金黄色球状颗粒,出厂类型为氢氧型。大孔型树脂是在聚合反应时加入致孔剂,形成多孔海绵状构造的骨架,内部和表面有大量永久性的微孔,再导入交换基团制成。这不仅为离子交换提供了好的接触条件,缩短了离子扩散的路程,还增加了许多活性中心。图2(a)为该树脂的SEM照片,从图2(b)的局部放大图像中可以清晰地观察到树脂表面大量的微孔。

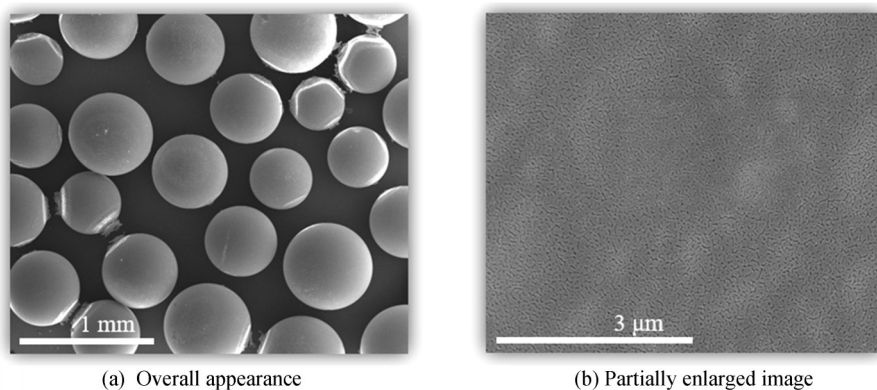


图2 阴离子交换树脂的SEM照片
Fig. 2 SEM images of anion exchange resin

该阴离子交换树脂在使用之前需要经过类型转换,使离子交换树脂吸附上 Br^- ,这一步骤是通过将阴离子交换树脂在 NaBr 水溶液中浸泡再烘干来完成的,经过类型转化即可得到 Br^- 型阴离子交换树脂,类型转化过程中发生的化学反应由式(1)表示。



其中,PS表示苯乙烯与二乙烯苯共聚形成的高分子网络骨架。该反应是液相中的离子和固相中离子间所进行的一种可逆性化学反应^[23],当液相中的某些离子被离子交换树脂吸附后,为维持水溶液的电中性,离子交换树脂将释放出等价离子回到液相溶液中^[24]。

3 实验结论与分析

3.1 改性后的晶体表面形貌及稳定性改善

为了证明经过离子交换树脂处理后 PQDs 晶体表面形貌的大幅改善,在热注入实验中通过使用被氧化的油酸铯前驱体溶液,最终合成的产物命名为“原始样品”,用 Br 型阴离子交换树脂处理后的样品命名为“改性样品”。图 3 为两者的实物和 TEM 对比照片,从图 3(a)可以清晰地观察到,原始样品呈现出与被氧化前驱体溶液类似的黄褐色。经过离子交换树脂处理后,如图 3(b)所示,改性样品呈现出透明的绿色,这是由于离子交换树脂内部大量的微孔使其具有与活性炭媲美的强吸附能力,可以选择性地吸附去除有机杂质。同时,从图 3(a)的 TEM 图像中还可以观察到,原始样品具有较差的表面形貌,主要表现为粒径尺寸差异大,边缘部分的晶粒粘连,且内部的晶粒排松散不规整,还有部分晶粒甚至未结晶为立方相。与之相比,从图 3(b)可以观察到,经过离子交换树脂处理后的改性样品呈现出清晰的立方相,而且晶粒完整排列整齐,几乎没有表面损伤或结构扭曲。图 3 右下为对应样品的高分辨 TEM 图像,高能电子束对微小区域内的样品进行逐行扫描时,结构稳定性较差的 PQDs 会由于高能电子束的轰击迅速氧化分解产生“黑点”,而这些“黑点”未在改性样品上观察到,并且可以观察到清晰的晶格条纹,这进一步说明改性样品中 PQDs 晶体具有更高的结晶度和更稳定的晶体结构。由于 PQDs 本身的离子晶体特性,离子交换树脂在去除多余有机物的同时,其交换基团上连接的 Br 会与 PQDs 晶体中的 Br 发生离子交换反应。卤素之间的交换并不会导致晶体粒径的大幅改变及相应的荧光发射光谱的中心波长移动。形貌较差的原始样品的晶体结构稳定性较低,而在离子交换反应进行中构成 PQDs 正八面体骨架的卤素离子需要先脱离原本的晶体结构,这将导致稳定性的进一步下降。所以这部分形貌较差的 PQDs 更容易被离子交换树脂选择性的去除,最终导致稳定性较高的完整晶胞单元被留在溶液中。

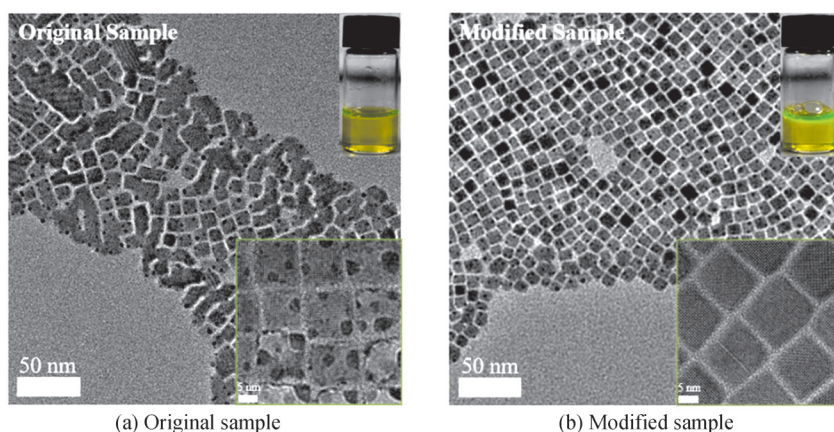


图 3 阴离子交换树脂处理前后 PQDs 的实物与 TEM 照片

Fig. 3 Physical and TEM images of PQDs before and after anion exchange resin treatment

为了证明离子交换树脂处理后的 PQDs 同时具有更加优异的稳定性,将原始样品和改性样品同时置于相同的环境条件下,分析了其 PL 光谱强度变化情况。持续的 UV 激发和高温环境都会导致 PQDs 部分晶相分离,同时还会使表面配体脱落进而导致晶粒团聚使得荧光强度减弱^[25]。如图 4 所示,经过连续 3 h 紫外 (Ultraviolet, UV) 光持续激发后原始样品和改性样品的发光强度分别衰减到原来的 80.6% 和 85.7%,经过连续 2 h 高温 70°C 加热后原始样品和改性样品的发光强度分别衰减到原来的 75.2% 和 99.6%。可以看出,改性样品的荧光强度衰减相对更少,表现出更加优异的稳定性。值得注意的是,经过高温加热后,改性样品的荧光强度几乎没有衰减,表现出了十分优异的热稳定性。这里,稳定性的提升同样得益于阴离子交换树脂的选择性去除作用,树脂的处理将结晶度低晶相不完整的 PQDs 去除后使得整体的稳定性得以提高。

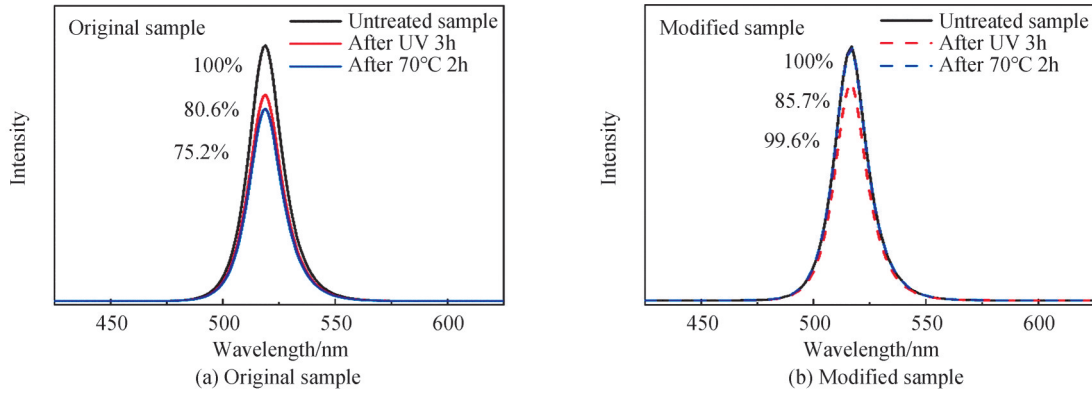


图4 阴离子交换树脂处理前后PQDs的稳定性对比光谱

Fig.4 Comparison spectrum of stability of PQDs before and after anion exchange resin treatment

3.2 改性后的荧光寿命与PLQY提升

除对表面形貌和稳定性的改善作用外,离子交换反应中过量的卤素会在PQDs表面形成一个自钝化层,帮助钝化PQDs上常见的表面缺陷,从而有效地抑制表面缺陷对光致载流子的俘获^[26],这一作用可以直观地反映在荧光寿命的变化上。图5为阴离子交换树脂处理前后PQDs的TRPL光谱,使用三阶指数衰减模型对曲线进行拟合,拟合数据及平均荧光寿命(τ_{avg})的计算公式汇总在表2中。

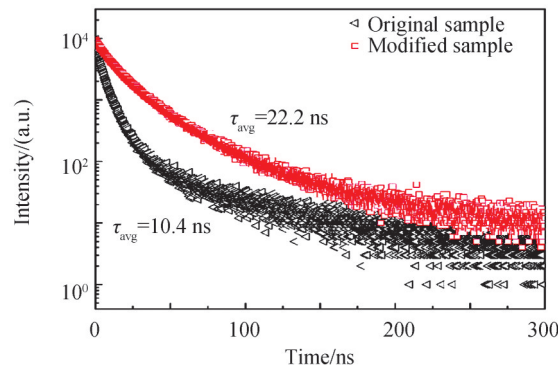


图5 阴离子交换树脂处理前后PQDs的TRPL光谱

Fig.5 TRPL spectrum of PQDs before and after anion exchange resin treatment

表2 TRPL光谱的各项拟合参数
Table 2 Fitting parameters of TRPL spectrum

Fitting parameters	Original sample	Modified sample
I_0	6.099	12.144
A_1	4 470.733	1 347.729
t_1/ns	2.010	2.840
A_2	5 187.528	6 255.789
t_2/ns	6.286	12.161
A_3	262.280	2 028.117
t_3/ns	33.975	34.181
R^2	0.999 59	0.999 61
τ_{avg}/ns	10.4	22.2
Fitting equation	$I(t) = A_1 e^{-t/t_1} + A_2 e^{-t/t_2} + A_3 e^{-t/t_3} + I_0$	
Calculation equation of τ_{avg}	$\tau_{avg} = \frac{A_1 t_1^2 + A_2 t_2^2 + A_3 t_3^2}{A_1 t_1 + A_2 t_2 + A_3 t_3}$	

拟合计算发现,离子交换树脂处理后 PQDs 的平均荧光寿命从 10.4 ns 提升到了 22.2 ns。平均荧光寿命计算公式中的参数 t_1 和 t_2 分别代表非辐射过程和辐射过程的相应寿命。晶体中的缺陷将作为非辐射复合的中心,从而抑制辐射复合过程,而最终平均荧光寿命的提高说明辐射复合是被增强的,这也从侧面反映出了缺陷态的减少,即较高的荧光寿命暗示着更少的表面缺陷态^[27]。平均荧光寿命的提升说明了阴离子交换树脂释放的过量卤素阴离子对 PQDs 表面缺陷态钝化和光学性质的改善做出了很大贡献。

图 6 为 PLQY 测试时的原始光谱,具体的计算方法由式(2)表示。

$$\text{PLQY} = \frac{\text{photons emitted}}{\text{photons absorbed}} = \frac{\int \left(\frac{\lambda}{hc} \right) \times [I_{\text{em}}^{\text{PQDs}}(\lambda) - I_{\text{em}}^{\text{ref}}(\lambda)] d\lambda}{\int \left(\frac{\lambda}{hc} \right) \times [I_{\text{ex}}^{\text{ref}}(\lambda) - I_{\text{ex}}^{\text{PQDs}}(\lambda)] d\lambda} \quad (2)$$

式中, $I_{\text{em}}^{\text{PQDs}}(\lambda)$ 和 $I_{\text{em}}^{\text{ref}}(\lambda)$ 分别表示测试样品和对比样品的发射强度, $I_{\text{ex}}^{\text{PQDs}}(\lambda)$ 和 $I_{\text{ex}}^{\text{ref}}(\lambda)$ 分别表示测试样品和对比样品的激发强度积分值。测试样品是经过稀释的 PQDs 溶液,对比样品是同体积的纯环己烷溶液。经计算,原始样品和改性样品的 PLQY 分别为 53.23% 和 90.00%。PLQY 如此大幅度的提升不仅仅是因为材料本身的直接带隙特性可以提高光吸收系数并加快辐射复合速率,另一个重要的原因是过量卤素阴离子对量子点表面缺陷的钝化,从而减少了大量的非辐射复合路径。

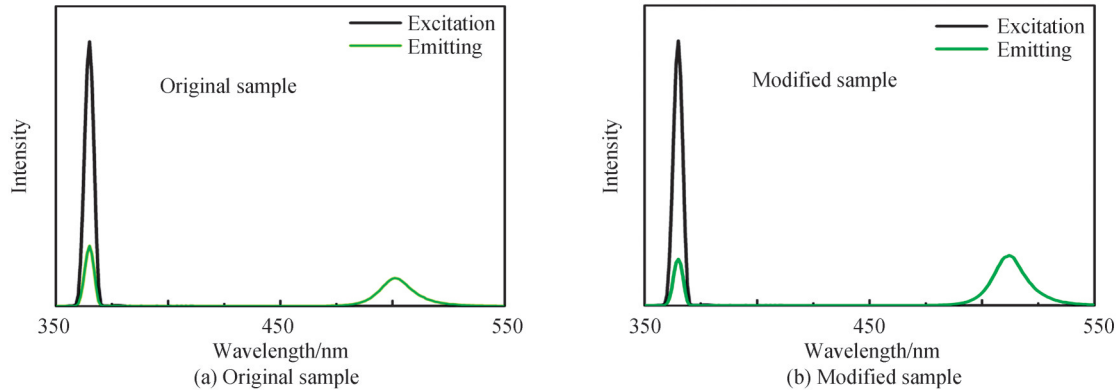


图 6 阴离子交换树脂处理前后 PQDs 的 PLQY 测试原始光谱

Fig. 6 Original spectra of the measured PLQY before and after anion exchange resin treatment

4 结论

基于阴离子交换树脂的强吸附特性和离子交换特性对 CsPbBr₃ PQDs 进行了改性研究,发现了阴离子交换树脂能够对表面形貌差、稳定性低的 PQDs 进行选择去除,改性后的 PQDs 表现出更高的稳定性和更优的晶体形貌。同时,阴离子交换树脂释放出的过量卤素阴离子可以钝化表面缺陷,从而提高 PQDs 的平均荧光寿命和 PLQY,阴离子交换树脂处理后的 PQDs 的荧光寿命分别从 10.4 ns 提高到 22.2 ns, PLQY 从 53.23% 提高到 90.00%。本研究证明了阴离子交换树脂能够对 CsPbBr₃ PQDs 进行形貌、寿命和性能的多重改善和提升,为 PQDs 的性能改善与稳定性提升提供了新的研究思路,阴离子交换树脂可再生和低成本的特性进一步扩展了该方法在光电领域中的应用前景。

参考文献

- [1] ZENG J, LI X, WU Y, et al. Space-confined growth of CsPbBr₃ film achieving photodetectors with high performance in all figures of merit[J]. *Advanced Functional Materials*, 2018, 28(43): 1804394.
- [2] YU J C, LEE A, KIM D B, et al. Enhancing the performance and stability of perovskite nanocrystal light-emitting diodes with a polymer matrix[J]. *Advanced Materials Technologies*, 2017, 2(6): 1700003.
- [3] YONG Z, GUO S, MA J, et al. Doping-enhanced short-range order of perovskite nanocrystals for near-unity violet luminescence quantum yield[J]. *Journal of the American Chemical Society*, 2018, 140(31): 9942-9951.
- [4] WANG H, ZHANG X, WU Q, et al. Trifluoroacetate induced small-grained CsPbBr₃ perovskite films result in efficient and stable light-emitting devices[J]. *Nature Communications*, 2019, 10(1): 665.
- [5] WANG H, LI X, YUAN M, et al. Fast postmoisture treatment of luminescent perovskite films for efficient light-emitting

- diodes[J]. *Small*, 2018, 14(15): 1703410.
- [6] YAO L J, FANG X, FANG D, et al. Research progress of the stability and photodetectors applications of organic-inorganic hybrid halide perovskite materials (invited) [J]. *Acta Photonica Sinica*, 2021, 50(1): 0150001
姚丽娟,方铨,房丹,等. 有机-无机杂化卤化物钙钛矿材料稳定性及其在光电探测器方面的研究进展(特邀)[J]. *光子学报*, 2021, 50(1): 0150001
- [7] PAN Q, HU H, ZOU Y, et al. Microwave-assisted synthesis of high-quality “all-inorganic” CsPbX₃ (X = Cl, Br, I) perovskite nanocrystals and their application in light emitting diodes[J]. *Journal of Materials Chemistry C*, 2017, 5(42): 10947-10954.
- [8] LI Z, MOON J, GHARAJEH A, et al. Room-temperature continuous-wave operation of organometal halide perovskite lasers[J]. *ACS Nano*, 2018, 12(11): 10968-10976.
- [9] LI Y, LV Y, GUO Z, et al. One-step preparation of long-term stable and flexible cspbbr₃ perovskite quantum dots/ethylene vinyl acetate copolymer composite films for white light-emitting diodes[J]. *ACS Appl Mater Interfaces*, 2018, 10(18): 15888-15894.
- [10] LI J, XU L, WANG T, et al. 50-fold EQE improvement up to 6.27% of solution-processed all-inorganic perovskite CsPbBr₃ QLEDs via surface ligand density control[J]. *Advanced Materials*, 2017, 29(5): 1603885.
- [11] HOYE R L Z, CHUA M R, MUSSELMAN K P, et al. Enhanced performance in fluorene-free organometal halide perovskite light-emitting diodes using tunable, low electron affinity oxide electron injectors[J]. *Advanced Materials*, 2015, 27(8): 1414-1419.
- [12] CHEN E G, LIN J Y, YANG T, et al. Asymmetric quantum-dot pixelation for color-converted white balance[J]. *ACS Photonics*, 2021, 8(7): 2158-2165.
- [13] XIE H X, CHEN E G, YE Y, et al. Highly stabilized gradient alloy quantum dots and silica hybrid nanospheres by core double shells for photoluminescence devices[J]. *The Journal of Physical Chemistry Letters*, 2020, 11(4): 1428-1434.
- [14] PROTESESCU L, YAKUNIN S, BODNARCHUK M I, et al. Nanocrystals of cesium lead halide perovskites (CsPbX₃, X = Cl, Br, and I): novel optoelectronic materials showing bright emission with wide color gamut[J]. *Nano Letters*, 2015, 15(6): 3692-3696.
- [15] KIM Y H, LEE H, KANG S, et al. Two-step-enhanced stability of quantum dots via silica and siloxane encapsulation for the long-term operation of light-emitting diodes[J]. *ACS Applied Materials & Interfaces*, 2019, 11(25): 22801-22808.
- [16] XU X J, WU Y Z, ZHU W H. Research progress on stability enhancement of CsPbX₃ perovskite and photovoltaic devices [J]. *CIESC Journal*, 2020, 71(9): 3933-3949.
许晓佳,吴永真,朱为宏. CsPbX₃钙钛矿材料与光伏器件稳定性强化研究进展[J]. *化工学报*, 2020, 71(9): 3933-3949.
- [17] WANG X T, FU Y H, NA G R, et al. Barium as doping element tuning both toxicity and optoelectric properties of lead-based halide perovskites[J]. *Acta Physica Sinica*, 2019, 68(15): 157101.
王雪婷,付钰豪,那广仁,等. 钡作为掺杂元素调控铅基钙钛矿材料的毒性和光电特性[J]. *物理学报*, 2019, 68(15): 157101.
- [18] CHEN W, HAO J, HU W, et al. Enhanced stability and tunable photoluminescence in perovskite CsPbX₃/ZnS quantum dot heterostructure[J]. *Small*, 2017, 13(21): 1604085.
- [19] LIU Z, LI F, HUANG G, et al. Stability improvement of photoluminescent QLEDs based on Mn-doped all-inorganic metal halide perovskite quantum dots with silica shell[J]. *Journal of Alloys and Compounds*, 2021, 888: 161505.
- [20] RAVI V K, SANTRA P K, JOSHI N, et al. Origin of the substitution mechanism for the binding of organic ligands on the surface of CsPbBr₃ perovskite nanocubes[J]. *The Journal of Physical Chemistry Letters*, 2017, 8(20): 4988-4994.
- [21] LIAN H W, KANG R, CHEN X Z, et al. Research progress on thermal stability of all inorganic perovskite CsPbX₃[J]. *Chinese Journal of Luminescence*, 2020, 41(8): 927-939.
练惠旺,康茹,陈星中,等. 全无机钙钛矿CsPbX₃热稳定性研究进展[J]. *发光学报*, 2020, 41(8): 926-939.
- [22] LUBER E J, MOBAROK M H, BURIK J M. Solution-processed zinc phosphide (α -Zn₃P₂) colloidal semiconducting nanocrystals for thin film photovoltaic applications[J]. *ACS Nano*, 2013, 7(9): 8136-8146.
- [23] PISMENSKAYA N, SARAPULOVA V, KLEVTSOVA A, et al. Adsorption of anthocyanins by cation and anion exchange resins with aromatic and aliphatic polymer matrices[J]. *International Journal of Molecular Sciences*, 2020, 21(21): 7874.
- [24] BARTON D N T, ROBSHAW T J, OKUSANYA O, et al. Remediation of radioiodine using polyamine anion exchange resins[J]. *Journal of Industrial and Engineering Chemistry*, 2019, 78: 210-221.
- [25] TRIVEDI S, PROCHOWICZ D, PARIKH N, et al. Recent progress in growth of single-crystal perovskites for photovoltaic applications[J]. *ACS Omega*, 2021, 6(2): 1030-1042.
- [26] LI X, WU Y, ZHANG S, et al. CsPbX₃ quantum dots for lighting and displays: room-temperature synthesis, photoluminescence superiorities, underlying origins and white light-emitting diodes[J]. *Advanced Functional Materials*, 2016, 26(15): 2435-2445.

- [27] MURZIN A O, SELIVANOV N I, KOZLOV V O, et al. Photoluminescence excitation spectroscopy of defect-related states in MAPbI₃ perovskite single crystals[J]. *Advanced Optical Materials*, 2020: 2001327.

Research on the Properties of CsPbBr₃ Quantum Dots Modified by Ion Exchange Resin

WANG Chenhui¹, CAI Junhu¹, HU Xinpei¹, CHEN Enguo^{1,2}, XU Sheng^{1,2}, YE Yun^{1,2},
GUO Tailiang^{1,2}

(1 *College of Physics and Information Engineering, Fuzhou University, Fuzhou 350108, China*)

(2 *Fujian Science & Technology Innovation Laboratory for Optoelectronic Information of China (Mindu Innovation Laboratory), Fuzhou 350108, China*)

Abstract: All-inorganic perovskite quantum dots have attracted much attention because of their outstanding photoelectric properties. However, the instability of PQDs to the environment has become a potential threat that restricts its practical application. At present, a large number of scientific studies have been devoted to improving the stability of PQDs. However, most of the current stability improvement schemes are to encapsulate PQDs in hydrophobic materials to provide a physical barrier against environmental changes, while the defects and unstable performance of materials themselves have not been effectively improved. It is therefore of great significance to study the corresponding performance and stability improvement schemes from the PQDs material itself. Ion exchange resin is a kind of polymer compound with a functional group, a network structure and insolubility. As for anion exchange resin, its active group can adsorb different types of anions to achieve ion exchange reaction, while PQDs is a kind of ionic compound containing halogen anions, and the two have a good binding ability. In this study, the performance and stability of CsPbBr₃ PQDs were improved simultaneously by introducing defect passivation and selective removal of ion exchange resin. The product PQDs prepared by high temperature thermal injection method was named as the original sample, and the sample treated with Br type anion exchange resin was named as the modified sample. From direct observation of their appearance, the original sample is yellow-brown, while the modified sample after ion exchange resin treatment is transparent green. The reason is the large number of micropores in the ion exchange resin, which has strong adsorption capacity comparable to activated carbon, and can selectively adsorb and remove organic impurities. TEM images show that the original sample has poor surface morphology. In contrast, the modified samples treated with ion-exchange resin show clear cubic phase with almost no surface damage or structural distortion. It is worth mentioning that continuous UV excitation and high temperature environment will lead to partial crystal phase separation of PQDs, and the surface ligand will fall off, resulting in grain agglomeration and decreased fluorescence intensity. The luminescence intensity of the original sample and the modified sample decreases to 80.6% and 85.7% respectively after 3 h of UV excitation, and to 75.2% and 99.6% respectively after 2 hours of 70°C heating. Obviously, the fluorescence intensity attenuation of the modified sample is relatively less, showing more excellent stability. It is worth noting that after high temperature heating, the fluorescence intensity of the modified sample almost does not decay, showing excellent thermal stability. Compared with the original sample, the modified sample also had a longer average fluorescence lifetime. The third-order exponential decay model was used to fit the fluorescence lifetime curve, and the results show that the average fluorescence lifetime of the original sample and the modified sample was 10.4 ns and 22.2 ns, respectively. The defects in the crystal will act as the center of non-radiation recombination to inhibit the radiation recombination process, and the increase of the final average fluorescence life indicates that the radiation recombination is enhanced, which also reflects the reduction of defect states from the side. The improvement of average fluorescence lifetime indicates that the excess halogen anions released by anion exchange resin contribute largely to the passivation of surface defects and the improvement of optical properties of PQDs. The PLQY of the original sample and the

modified sample were 53.23% and 90.00%, respectively. Such a large increase in PLQY is not only due to the direct band gap characteristics of the material itself, which can improve the light absorption coefficient and speed up the radiation recombination rate, but also due to the passivation of excessive halogen anions on the surface defects of quantum dots, thus reducing a large number of non-radiation recombination paths. In summary, the introduction of ion exchange resin can selectively remove PQDs single crystals with poor morphology and unstable structure without changing the inherent crystal phase of PQDs, which makes the surface morphology and uniformity of the prepared PQDs greatly improved. And the stability of PQDs has also been greatly improved under long-term ultraviolet light and high temperature experiments. Moreover, before and after modification, the photoluminescence quantum yield and fluorescence lifetime of CsPbBr₃ PQDs were significantly increased from 53.23% to 90.00% and from 10.4 ns to 22.2 ns, respectively. This research provides a new idea for improving the performance and stability of PQDs. Due to the reproducible and low-cost characteristics of ion exchange resins, it has broad application prospects in the field of optoelectronics.

Key words: Perovskite quantum dots; Ion exchange resin; Defect passivation; Selective adsorption; Performance improvement

OCIS Codes: 160.2220; 040.5160; 230.5160