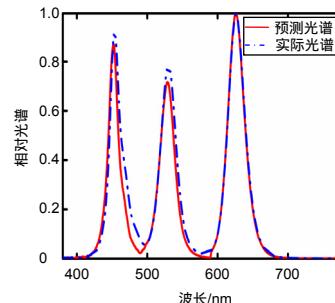




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量子点白光 LED 光谱拟合方法的研究

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摘要: 量子点材料具有发光光谱窄、发光波长可调及荧光量子产率高等特点, 其制成的发光器件在提升色域方面更具潜力。本文介绍了一种由蓝光 LED 激发 CdSe 红、绿光量子点并结合表色系统计算方法配得白光的计算方法。经多次实验确定, 红、绿光量子点与胶水配比为(1 : 60)和(1 : 10), 胶量测试范围为 $1.4 \mu\text{L} \sim 2.2 \mu\text{L}$ 和 $3.0 \mu\text{L} \sim 5.0 \mu\text{L}$ 。采用传统 LED 制作方式和分层结构制得样品, 测试此胶量范围对蓝光的吸收、转化比率, 经 Matlab 拟合得到胶量与吸收、转化率的函数关系。取上述测试胶量范围形成的白光区域点(0.34, 0.3), 得到红、绿光量子点胶量为 $1.9 \mu\text{L}$ 和 $4.55 \mu\text{L}$, 根据光谱计算公式得到对应的理论光谱。再根据上述胶量制作验证样品, 测试得到色坐标点为(0.3409, 0.2992)且对应的光谱与理论光谱也基本重合。

关键词: 量子点; 白光 LED; Matlab; 光谱拟合

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Study on spectral fitting method of quantum dot white LED

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Abstract: Quantum dot materials have the characteristics of narrow luminescence spectrum, adjustable luminescence wavelength and high fluorescence quantum yield. The quantum dot LEDs have more potential in improving color gamut. In this paper, a method of white light generation by blue LED excited CdSe red and green quantum dots is introduced. The ratio of red and green quantum dots to glue was (1 : 60) and (1 : 10), and the test range of glue content was $1.4 \mu\text{L} \sim 2.2 \mu\text{L}$ and $3.0 \mu\text{L} \sim 5.0 \mu\text{L}$. The samples were prepared by traditional method and layered structure. The absorption and conversion ratio of blue light in the range of glue amount were tested. The function relationship between glue amount and absorption and conversion was obtained by Matlab fitting. When taking the dots (0.34, 0.3) in white light region formed in the above test glue amount range, the red and green quantum dots were calculated with glue amount of $1.9 \mu\text{L}$ and $4.55 \mu\text{L}$, and the corresponding theoretical spectrum was established according to the spectral calculation formula. According to the above glue amount, the verification

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samples were made and tested the color coordinates (0.3409, 0.2992) and the homologous spectra were basically coincident with the theoretical spectra.

Keywords: quantum dots; white LED; Matlab; spectral fitting

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1 引言

21世纪是一个信息与显示时代，显示技术无处不在，如智能手机、电脑等都与显示技术息息相关^[1]。目前，用做显示背光源的白光LED主要由蓝光LED芯片与一种或多种荧光粉组合而成，芯片发出的蓝光与激发荧光粉获得的黄光混合得到白光^[2]。显示应用希望拥有高颜色饱和度，用于白光LED的荧光粉(如YAG:Ce⁺)大都具有较宽的发射光谱，而减小发射光谱带宽能够增大显示器色域、提高饱和度。因此，窄光谱发射的荧光材料成为背光领域研究热点^[3]。

量子点是指在空间三个维度上存在量子限域效应的半导体晶体材料，又被称为“人造原子”^[4-5]。与传统荧光粉相比，半导体量子点作为一种新型波长转换材料具有发射光谱窄^[6]、量子产率高、容易与器件集成等优良特性^[7-8]，并且可以通过改变尺寸来调控其光学和电学性质^[9-11]。量子点背光因其RGB三色的半峰宽窄，色纯度高，因而可以实现更高的色域，可以实现NTSC110%的色域^[12]。近期，南京理工大学学报报道了使用绿色和红色CsPbX₃PeQDs/PMMA薄膜作为荧光转换材料的白光LED器件，得到的色域显著大于NTSC的标准色域^[13-14]。韩国学者报道了蓝光LED激发5种颜色无机钙钛矿量子点的白光LED，色域达到了NTSC标准色域的145%^[15]。

目前，针对光谱叠加的研究较多，如通过光功率谱的配比得到高显色性白光^[16]，但未结合实际生产中荧光粉质量比加以验证。本文利用蓝光激发CdSe红光和绿光量子点得到白光，测得不同量的量子点对应的光功率谱，通过Matlab拟合出红、绿光量子点胶体用量与吸收率、转化率关系式，利用光谱叠加原理拟合出白光，经实际配量测出的光谱与理论光谱基本一致，这对于今后的实际配粉工作具有一定指导作用。

2 实验原理与过程

2.1 实验原理

量子点光致发光原理^[16]是量子点材料吸收光子后电子跃迁产生新的光子。材料在吸收光子后产生辐射

复合与非辐射复合两个过程，新的光子产生于辐射复合过程，故新光子存在一定的转化效率。本实验将量子点与胶水的混合物作为研究对象，故考虑利用量子点胶体对蓝光的吸收率与其转化成红、绿光的转化率进行光谱计算。

实验样品结构如图1所示，测试得到红、绿光量子点胶量对蓝光的吸收率 α 及转化率 β ，通过Matlab计算拟合吸收、转化率与胶量的最优函数关系式。红绿蓝三色光的光功率计算方法如式(1)~式(3)所示：

$$P_2 = P_0 \times \alpha_0 \times \beta_0 , \quad (1)$$

$$P_4 = (P_0 - P_0 \times \alpha_0) \times \alpha_1 \times \beta_1 , \quad (2)$$

$$P_3 = P_0 - P_0 \times \alpha_0 - (P_0 - P_0 \times \alpha_0) \times \alpha_1 , \quad (3)$$

其中： P_2 为红光光功率， P_0 为蓝光初始光功率， α_0 为红光量子点吸收率， β_0 为红光量子点转化率； P_4 为绿光光功率， α_1 为绿光量子点吸收率， β_1 为绿光量子点转化率； P_3 为蓝光所剩光功率。白光绝对光谱计算方法如式(4)所示：

$$P(\lambda) = P_1(\lambda) \times P_3 + P_2(\lambda) \times P_4 + P_3(\lambda) \times P_2 , \quad (4)$$

其中： $P(\lambda)$ 为白光绝对光谱， $P_1(\lambda)$ 为蓝光相对光谱， $P_2(\lambda)$ 为红光相对光谱， $P_3(\lambda)$ 为绿光相对光谱。

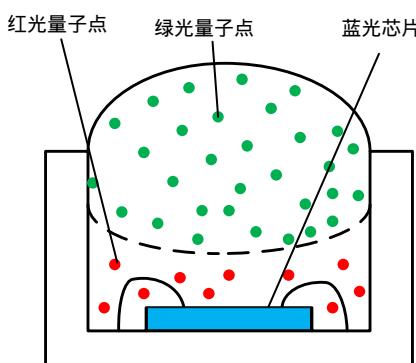


图1 实验结构图

Fig. 1 Structure simulated in this work

由白光光谱 $P(\lambda)$ 得到对应的色坐标点，则需要引入国际照明委员(CIE)1931XYZ表色系统计算方法^[17]：

$$x = X / (X + Y + Z) , \quad (5)$$

$$y = Y / (X + Y + Z) , \quad (6)$$

$$z = Z / (X + Y + Z) , \quad (7)$$

$$x + y + z = 1 , \quad (8)$$

其中： x, y, z 为色坐标， X, Y, Z 为人眼对于红、绿、蓝色感知强度，它们分别为

$$X = K \int_{380}^{780} P(\lambda) \bar{X}(\lambda) d\lambda = K \sum_{\lambda=380}^{780} P(\lambda) \bar{X}(\lambda) \Delta\lambda , \quad (9)$$

$$Y = K \int_{380}^{780} P(\lambda) \bar{Y}(\lambda) d\lambda = K \sum_{\lambda=380}^{780} P(\lambda) \bar{Y}(\lambda) \Delta\lambda , \quad (10)$$

$$Z = K \int_{380}^{780} P(\lambda) \bar{Z}(\lambda) d\lambda = K \sum_{\lambda=380}^{780} P(\lambda) \bar{Z}(\lambda) \Delta\lambda , \quad (11)$$

$$K = \frac{100}{\sum_{\lambda=380}^{780} P(\lambda) \bar{Y}(\lambda) \Delta\lambda} , \quad (12)$$

其中： $P(\lambda)$ 光源光谱功率分布， $X(\lambda)、Y(\lambda)、Z(\lambda)$ 为颜色匹配函数， K 为调整系数。

2.2 实验过程

- 1) LED 芯片与支架焊接，并打线。
- 2) 分别测得蓝光 LED 芯片、红、绿光量子点的相对光谱： $P_1(\lambda)、P_2(\lambda)、P_3(\lambda)$ 。
- 3) 测出蓝光芯片初始光功率为 P_0 。
- 4) 量子点与环氧按比例混合均匀，在蓝光芯片上利用点胶机点入一层红光量子点胶体(胶量： x)，计算拟合得到红光量子点对蓝光的吸收率函数 $\alpha_0=f_{R1}(x)$ ，转化率函数 $\beta_0=f_{R2}(x)$ 。

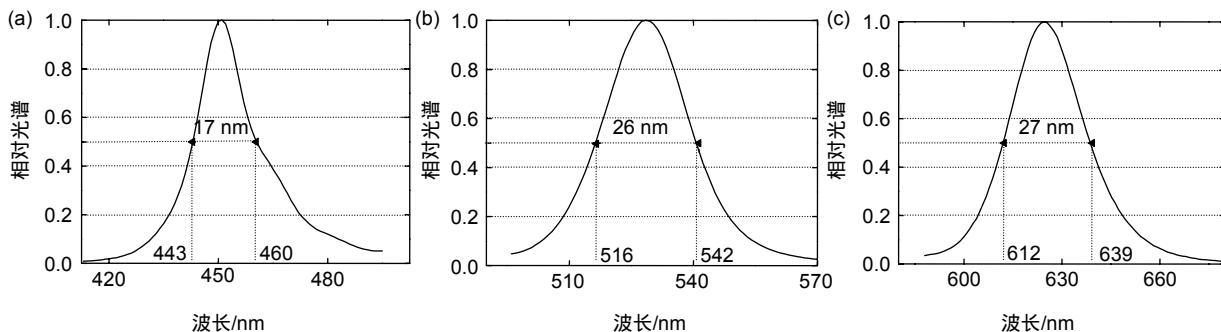


图 2 (a) 蓝光芯片相对光谱；(b) 绿光量子点相对光谱；(c) 红光量子点相对光谱

Fig. 2 (a) Blue chip relative spectrum; (b) Green quantum dots relative spectrum; (c) Red quantum dots relative spectrum

表 1 不同量子点胶量的吸收和转化率
Table 1 Absorption and conversion of different quantum dot gels

红光量子点胶量/ μL	1.4	1.6	1.8	2.0	2.2
红光量子点吸收率	0.5420	0.5611	0.5826	0.5968	0.6022
红光量子点转化率	0.1715	0.1815	0.2075	0.2191	0.2282
绿光量子点胶量/ μL	3.0	3.5	4.0	4.5	5.0
绿光量子点吸收率	0.7327	0.7639	0.7865	0.8055	0.8257
绿光量子点转化率	0.2085	0.21543	0.2077	0.2038	0.2030

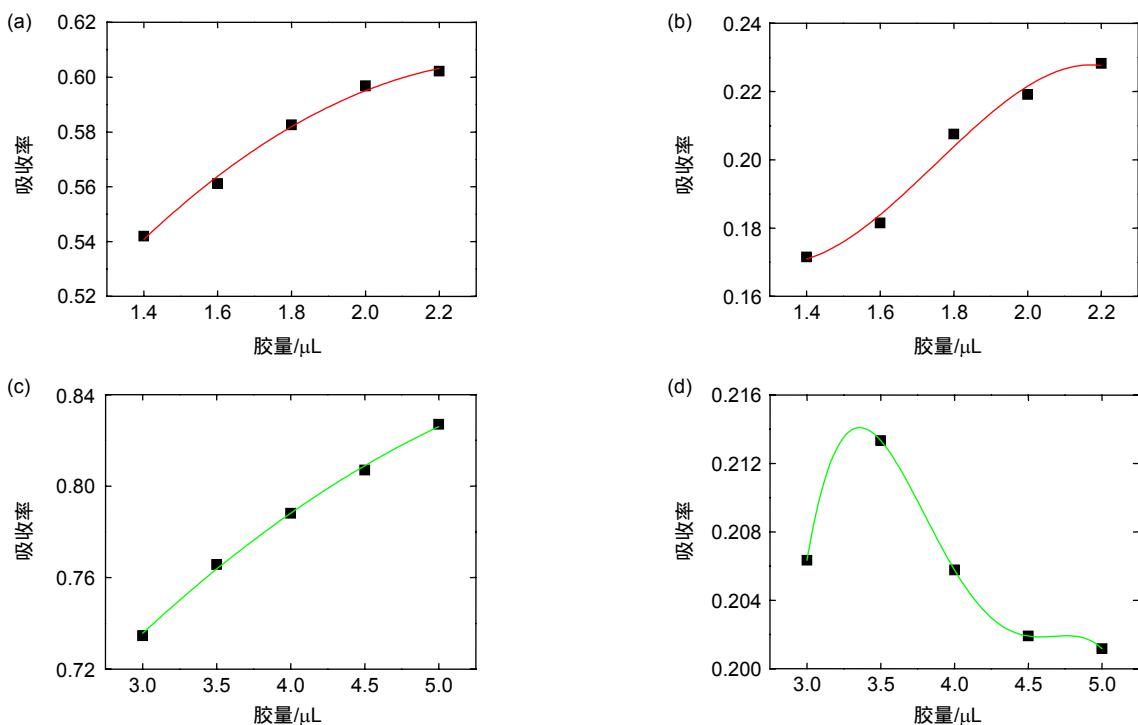


图 3 (a) 红光量子点吸收率拟合曲线; (b) 红光量子点转化率拟合曲线;
(c) 绿光量子点吸收率拟合曲线; (d) 绿光量子点转化率拟合曲线

Fig. 3 (a) Red quantum dot absorption rate fitting curve; (b) Red quantum dot conversion rate fitting curve;
(c) Green quantum dot absorption rate fitting curve; (d) Green quantum dot conversion rate fitting curve

图 3(d) 曲线得到绿光量子点转化率数：

$$f_{G2}(y) = -0.0126y^4 + 0.21281y^3 - 1.3368y^2 + 3.6827y - 3.5381。$$

取红、绿光量子点胶量最大、最小值的 4 种组合计算得到对应的吸收、转化率，再由式(1)~式(4)计算出光谱，将光谱带入式(5)~式(12)计算得到边界点的色坐标值： $A_2(0.4006, 0.3009)$ ， $A_2(0.3327, 0.3102)$ ， $A_3(0.3027, 0.2508)$ ， $A_4(0.3661, 0.2603)$ ，得到色坐标计算区域如图 4 所示。

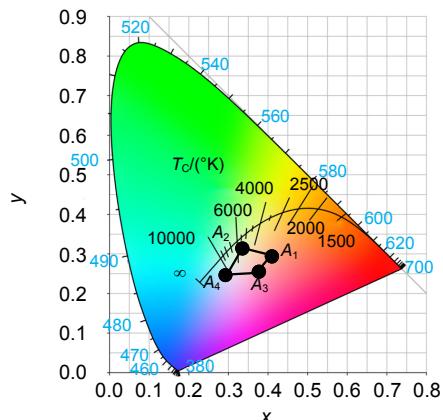


图 4 色坐标计算区域

Fig. 4 Color coordinate calculation area

验证理论计算的准确性，取色坐标为(0.34, 0.3)，利用色坐标计算式(5)~式(12)及红、绿光量子点吸收、转化函数反推得到红、绿光量子点胶量分别为 1.52 μL 和 4.65 μL ，得到预测光谱与实际光谱如图 5 所示。理论计算与实际光谱偏差太大，考虑以下两种原因引起误差：一是在制作测试样品过程中红光量子点经过两次加热，引起量子点缺陷暴露，导致光谱误差较大，二是不同胶量对于出光的影响。

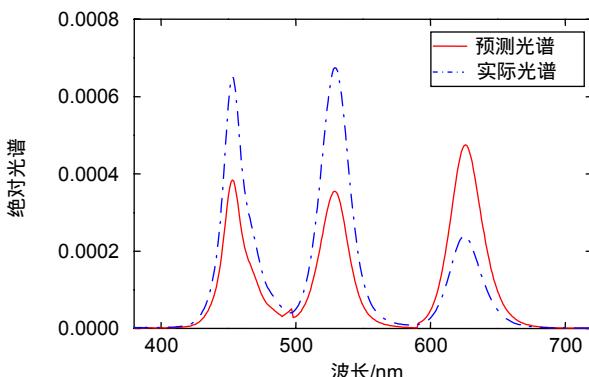


图 5 预测光谱与实际光谱

Fig. 5 Predicted and actual spectral

3.2 实验误差验证分析

验证红光量子点加热两次损失情况：通过在烘箱里加热，对比一次加热和两次加热的红光光功率，如图 6(a)所示，发现红光光功率衰减约 5%，可认为上述误差不是由红光量子点二次加温导致的。

验证不同胶量对于出光的影响：经光学显微镜观察不同样品发现，胶量少时样品表面形成凹面，胶量多时样品表面形成凸面，结构如图 6(b)所示。取两个不同白胶胶量分别制得凹凸面样品，测试结果如图 6(c)所示。分析原因为：蓝光经过凹表面时易发生全反射，蓝光出光减少，红光量子点吸收的蓝光增加；蓝光经

过凸表面时减少全反射发生，蓝光出光增加，红光量子点吸收的蓝光减少。因此，实验过程中需要考虑红光量子点胶量与绿光量子点胶量的相互影响。

3.3 改进过程及结果

之前实验分析仅以红、绿光量子点的量作为自变量来计算获得红、绿量子点吸收、转化率。但实验发现胶水量对于出光也有较大影响，故而改进实验将红、绿光量子点的量和白胶胶量作为自变量来拟合红、绿光量子点的吸收、转化率。采用一种量子点胶量对应五种白胶胶量的方法，制得样品并测试得到吸收、转化率与胶量的关系如图 7 所示。

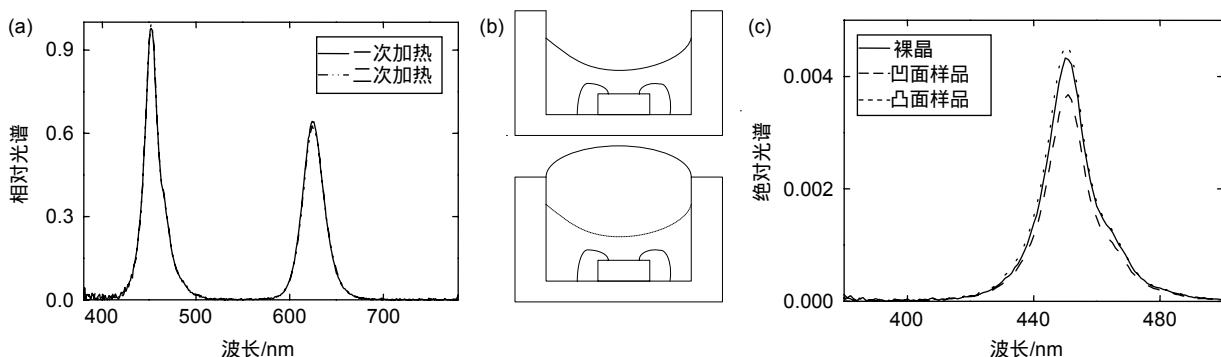


图 6 (a) 红光量子点两次加热影响; (b) 凹、凸面样品示意图; (c) 凹凸面对于蓝光出光影响

Fig. 6 (a) Twice heating effect of red quantum dot;

(b) Concave and convex sample schematic; (c) The concave and convex surface affects the blue light

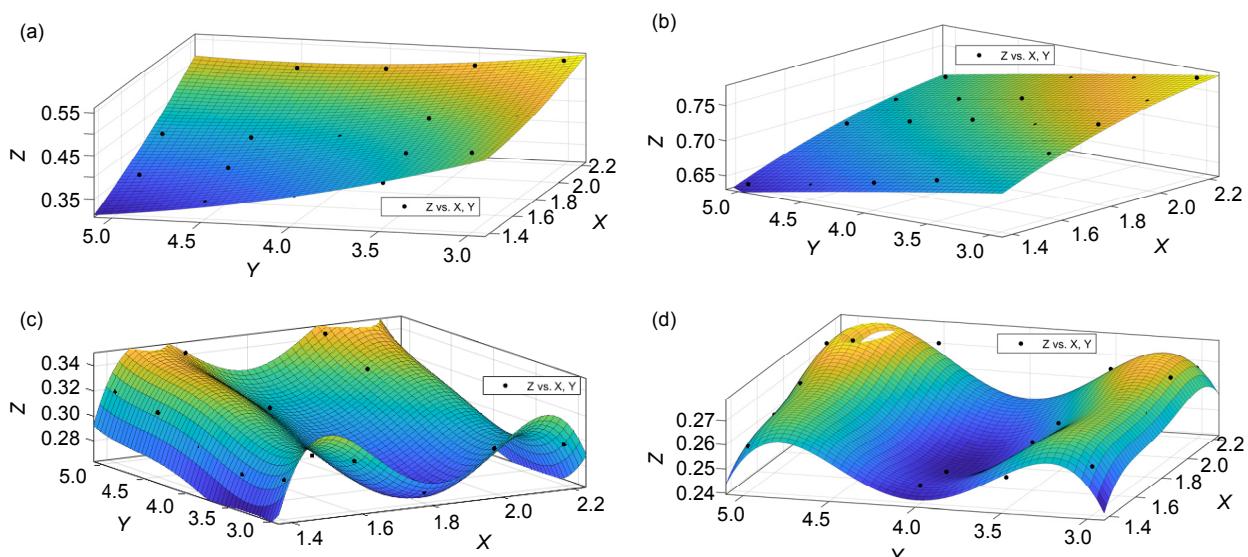


图 7 (a) 红光量子点吸收率拟合曲面; (b) 红光量子点转换率拟合曲面;

(c) 绿光量子点吸收率拟合曲面; (d) 绿光量子点转换率拟合曲面

Fig. 7 (a) Red quantum dot absorption rate fitting surface; (b) Red quantum dot conversion rate fitting surface;

(c) Green quantum dot absorption rate fitting surface; (d) Green quantum dot conversion rate fitting surface

图 7(a)曲面为红光量子点吸收率函数 :

$$Z_{R1}(x,y)=1.3211-0.3534x-0.3059y \\ +0.0703x^2+0.0637xy+0.0177y^2;$$

图 7(b)曲面为红光量子点转换率函数 :

$$Z_{R2}(x,y)=-1.4401-15.0701x+9.4111y \\ +13.9601x^2-1.8301xy-3.314y^2-4.9641x^3 \\ -0.0101x^2y+0.5038xy^2+0.4971y^3+0.6375x^4 \\ +0.0432x^3y-0.0318x^2y^2-0.0343xy^3-0.0278y^4;$$

图 7(c)曲面为绿光量子点吸收率函数 :

$$Z_{G1}(x,y)=0.5188+0.1145x-0.0457y-0.0101x^2-0.0101y^2;$$

图 7(d)曲面为绿光量子点转化率函数 :

$$Z_{G2}(x,y)=-20.8501+14.8101x+15.9401y \\ -5.2221x^2-2.1771xy-11.2401y^2+0.8465x^3 \\ +0.2501x^2y+0.6439xy^2+3.7921y^3-0.0501x^4 \\ -0.0042x^3y-0.0536x^2y^2-0.0401xy^3-0.5131y^4.$$

取红、绿光量子点胶量最大、最小值的 4 种组合计算得到对应的吸收、转化率，再由式(1)~式(4)计算出光谱，将光谱带入式(5)~式(12)计算得到边界点的色坐标值： $B_1(0.3648, 0.3003)$ ， $B_2(0.3327, 0.3102)$ ， $B_3(0.3203, 0.2719)$ ， $B_4(0.3637, 0.2662)$ ，得到色坐标计算区域如图 8 所示。

验证理论计算的准确性，取色坐标为(0.34, 0.3)，利用色坐标计算式(5)~式(12)及红、绿光量子点吸收、转化函数反推得到红光和绿光胶量分别为 $1.9 \mu\text{L}$ 和 $4.55 \mu\text{L}$ ，得到预测光谱与实际光谱如图 9(a)所示，实际与预测光谱数据基本吻合。根据光谱数据计算得到预测光谱色坐标为(0.3409, 0.2992)，实际光谱色坐标为(0.3280, 0.3077)，如图 9(b)所示，计算与实际色坐标误差非常小；样品点亮前后的实际效果如图 9(c)所示。

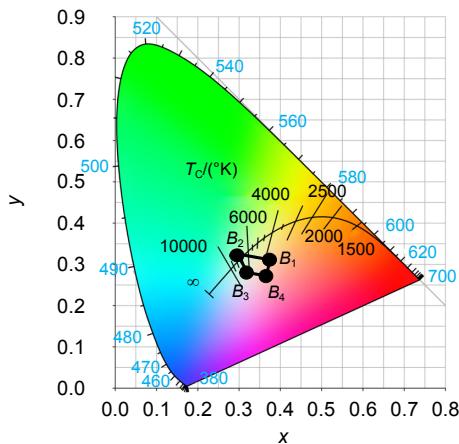


图 8 色坐标计算区域

Fig. 8 Color coordinate calculation area

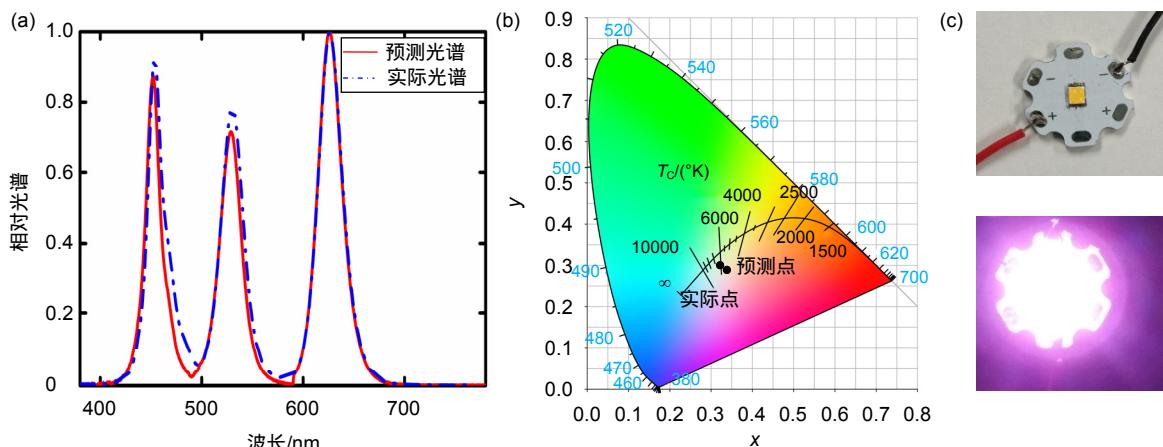


图 9 (a) 预测与实际光谱; (b) 预测与实际色坐标点; (c) 样品点亮前后效果图

Fig. 9 (a) Prediction and actual spectrum; (b) Prediction and actual coordinates; (c) Sample before and after lighting

4 总结与展望

本文采用蓝光激发 CdSe 红、绿光量子点制得量子点白光 LED。通过理论计算出白光光谱，结合量子点配粉验证光谱，确定出白光光谱与实际量子点粉及胶量之间的函数关系，最终得到理论光谱与实际光谱基本一致。本文只考虑白光光谱拟合的一致性，而未考虑最终样品的光效、显色指数及色温等性能参数，所以后续实验将继续深入研究。

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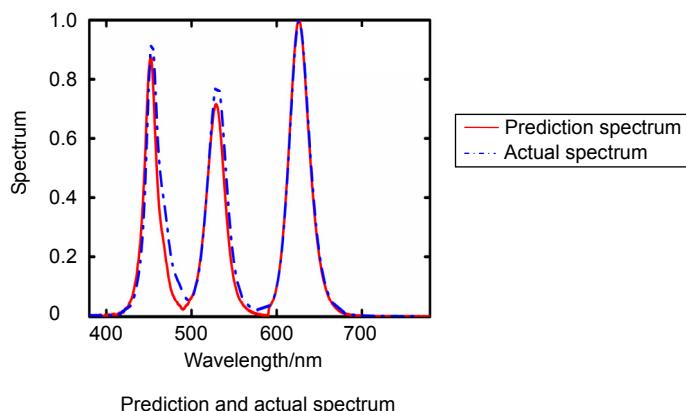
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Study on spectral fitting method of quantum dot white LED

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Overview: Quantum dot material is a new semiconductor luminescent material which has the characteristics of narrow luminescent spectrum, adjustable luminescent wavelength and high quantum yield. Because of its narrow fluorescence spectrum, the light-emitting device is very helpful to improve the color gamut and saturation in the backlight field. Quantum dot materials are used as backlight devices to improve the color gamut and saturation which need to match the white light to meet the requirements through the principle of three primary colors. At present, there are many studies on the fitting method of white light spectrum, but it is not verified by the quality ratio of fluorescent materials in actual production. Based on the CIE 1931 XYZ surface color system, a new white light spectrum fitting method is developed in this paper.

The ratio of red and green QDs to glue was (1: 60) and (1: 10). The test range of the glue content was 1.4 μL ~2.2 μL and 3.0 μL ~5.0 μL . In the experiment, the traditional LED manufacturing method is used and the red green quantum dots are excited by the characteristics of blue light short wavelength and high energy to obtain the red green blue three colors which are mixed into white light. At the same time, due to the more stable nature of red quantum dots, the layered structure of red quantum dots under green quantum dots is adopted. Make samples according to the above-mentioned manufacturing method, test the absorption and conversion ratio of different samples to blue light, get the functional relationship between glue amount and absorption and conversion ratio through Matlab fitting, and then substitute it into the calculation formula to get the white light area. In the experiment, it is found that the amount of red-green quantum dots with layered structure will affect each other's absorption conversion; therefore, when fitting the functional relationship between the amount of glue and the absorption conversion, it is necessary to take the amount of red-green quantum dots as an independent variable at the same time.

According to the spectral fitting method, the white light region of each sample in the color coordinate is calculated, and a point (0.34, 0.3) in the region is taken. The corresponding red and green quantum dots are 1.9 μL and 4.55 μL by the inverse use of the spectral fitting method, so the corresponding theoretical spectrum is obtained. Then, according to the above-mentioned amount of glue, the white light spectrum is obtained, which basically coincides with the theoretical spectrum, and the color coordinate points (0.3409, 0.2992) obtained from the actual spectrum are also basically close. The fitting method of white light spectrum introduced in this paper is combined with the actual production and verified, which has a certain reference value for the preparation of white light of photoluminescent products.

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