第十三届“挑战杯”全国大学生课外学术科技作品竞赛

科技发明制作 B 类

基于新型铜铟硫纳米晶的白光LED与光转换膜的制备和应用

周青超

肖　静

李东海

李俊飞

郭旭祯

原　泉

2013 年 6 月

基于新型铜铟硫纳米晶的白光LED与光转换膜的制备和应用

摘要

铜铟硫($CuInS_2$)纳米晶是近年来发展起来的一种新型半导体纳米晶材料，具有发射光谱宽、波长易于调控、量子产率高、合成成本低、容易与封装材料复合等优点，本作品利用非注入法制备了性能优异的具有不同发光波长的$CuInS_2$纳米晶材料，将其作为荧光粉应用到荧光转换型白光LED的光转换层中，有效地提高了白光LED的显色性能，制备出了显色指数超过90、色温在3000-11000 K可调的大功率白光LED，能够满足室内照明的各项要求，基于此的暖白光LED是本作品的亮点之一。在此基础上，本作品制备的基于$CuInS_2$纳米晶的光转换膜具有色散小、稳定性好的优点，满足Remote LED器件、显示用背光源等诸多领域的应用要求，具有巨大的市场潜力。

关键词：$CuInS_2$；纳米晶；白光LED；显色指数；光转换膜；农用补光

Abstract

$CuInS_2$-based semiconductor nanocrystals have low toxicity, tunable emissions in the wavelengths of the visible to near infrared region, large absorption band, high emission intensities and easy-encapsulation, therefore, it can be an excellent substitute for conventional phosphor powder in fabricating high-luminescent white light-emitting diodes (WLEDs). Here we report the synthetic chemistry of solid state $CuInS_2$ phosphor powder with the non-injection method. We successfully obtain the white LED with high color rendering index over 90 and Color Correlated Temperature (CCT) ranging from 3000 K to 11000 K, which all meet the requirements of indoor lighting, especially the warm white LED based on this is one of the highlights of this work. Furthermore, we prepared a simple and effective optical conversion film fabricated by $CuInS_2$ nanocrystals, which has lower dispersion and better thermal stability. These advantages can meet Remote LED devices, display backlight, and many other fields of application requirements, possessing with huge market potential.

Keywords: $CuInS_2$; Nanocrystals; White LED; Color Rendering Index; Optical conversion film; Farm complement

目录

1. 研究背景

近年来，能源和环境问题日益严重，节能低碳已然成为社会发展的必然趋势。照明和显示消耗的电量超过了全球发电量的20%[1]，因此寻求高效率发光技术成为科学界和工业界关注的热点课题[2,3]。白光LED是新一代固态发光技术，具有高效节能、绿色环保等优点，已经在舞台照明、液晶显示、广告宣传等领域中得到广泛应用。最近，包括中国在内的多个国家颁布了逐步淘汰白炽灯路线图。荧光转换型白光LED技术相对成熟，是替代白炽灯的极佳选择[3]。因此，LED拥有着庞大的市场空间，具有巨大的经济潜力，与LED相关的材料和技术研究受到国内外的高度重视。我国《“十二五”节能环保产业发展计划》中明确提出加快半导体固体照明（LED、OLED）的研发，白光LED的研究作为战略性新型产业目前正处于关键的转型阶段。纳米科学与技术的发展提供了种类繁多的光电功能材料和应用技术，国家中长期科技发展纲要中也将纳米研究列为四个重大科学研究计划之一，提出重点研究纳米材料的可控制备及其在能源、环境、信息、医药等领域的应用，利用半导体纳米晶制备的新型光电器件是目前科学和技术发展的前沿。例如，2011-2013年，Nature Photonics期刊多次报道纳米晶LED的研究进展，还专门讨论过纳米晶代替稀土发光材料的可能性[4-7]；2013年初Sony公司展示了一款基于纳米晶LED的高清液晶电视，受到了广泛关注，Nature杂志专门进行了报道[8]。

2. 研究意义

白光LED的性能主要是由芯片和荧光粉来决定。目前普遍使用的稀土类荧光粉材料本身存在诸多问题，不能满足高效、高亮度、低成本、暖白光二极管的要求。再者，稀土类荧光粉的专利大都被国外大公司覆盖和垄断，中国作为白光LED生产大国亟需自主研发的白光LED荧光粉技术[9]。

半导体纳米晶是一类新兴的颜色可调的光转换材料[10]，具有溶液法制备、容易分散、发光光谱可调、发光效率高等优点，有希望改变传统荧光粉材料选择的局限和提高现有白光LED的性能，成为LED荧光粉的候选材料。传统的CdSe类纳米晶含有重金属离子，限制了其在白光LED中的应用[11]。$CuInS_2$纳米晶是一类不含重金属的新型低毒荧光粉材料，具有尺寸小、发射光谱宽、波长可调、

Stokes位移大、合成成本低等显著优点，在白光LED中应用优势明显。作者所在实验室在此方面有很好的基础，通过尺寸、组分和表面调控策略，对材料的合成工艺进行了优化，获得了一系列高荧光量子产率的纳米晶材料。本作品在以上材料开发的基础上，开展$CuInS_2$纳米晶材料在白光LED和光转换膜中的应用，制备出高显色指数的暖白光LED和多功能的光转换膜原型器件，并对其应用领域进行了探索。

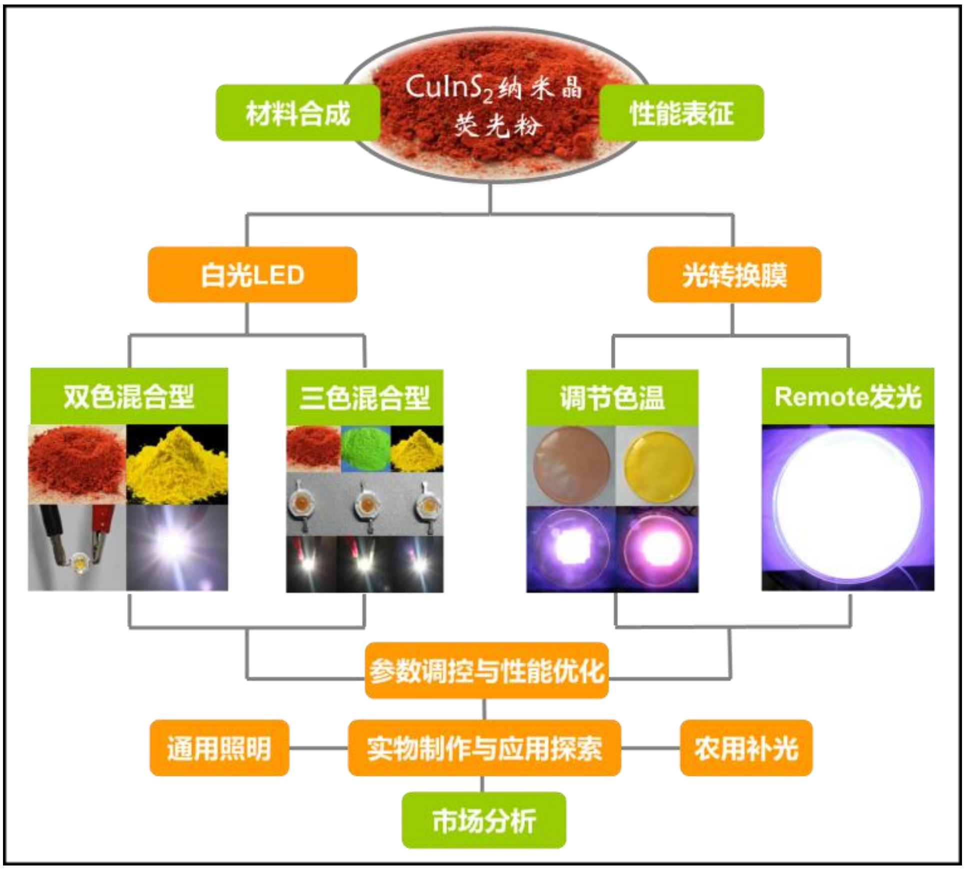
3. 创新点

(1) $CuInS_2$纳米晶具有很宽的发射光谱，本作品将红色发光的$CuInS_2$纳米晶与传统荧光粉共同使用，制备出高显色指数、暖白光 LED，主要参数如下：效率45-60lm/W，显色指数达93，色温3000-11000 K可调；
(2) $CuInS_2$纳米晶尺寸小、单分散性好，本作品将$CuInS_2$纳米晶与PMMA共混制得光转换膜，并制备出Remote结构白光LED；
(3) 提出一种利用不同颜色的光转换膜组合制作而成的灯具，通过简单操作即可调整灯光的色温，具有实用价值；利用光转换膜可发光波长可调的特性，制作出一种可调节灯光波长范围的农用补光照明系统，可满足农作物在不同生长阶段对光线波长的不同需求。

4. 研究思路

本作品主要针对$CuInS_2$纳米晶的LED应用开发开展，主要研究思路如示意图1所示。白光LED中的红色荧光粉在普通室内照明所需的暖色光中发挥着举足轻重的作用[12,13]。目前普遍使用的氮化物荧光粉价格昂贵（300~500 元/克），本作品采用的$CuInS_2$纳米晶，成本较低（合成成本仅10元/克）。有文献报道[14–22]，在荧光转换型白光LED中加入 CdSe/ZnS，CdS:Cu/ZnS 半导体纳米晶能够改善显色质量。然而，众所周知，镉具有毒性，所以基于镉的半导体纳米晶的发展受到限制。最近的研究发现，基于$CuInS_2$的半导体纳米晶具有低毒性的特点，是含镉半导体纳米晶的良好替代品[23–27]。尤其是$CuInS_2$半导体纳米晶，具有很宽的发射光谱，其半峰宽为100-200 nm，并且具有较大的斯托克斯位移(200-300 meV)，可对其发射光谱进行精确调节[28]。在白光LED的应用中，这些显著的特点有利于提

高显色性能和调节色温，为制备“室内小太阳”——高显色性暖白光LED提供了可能。



在上述研究的基础上，我们发现上述组合方式采用的是传统白光LED封装方式[9]，即将荧光粉混合在封装材料中，然后点在芯片上，加热固化，形成荧光粉涂层。其缺陷在于：荧光材料比重大，颗粒较大，极易沉淀，因此在点样到完全固化整个过程中，容易造成荧光材料下沉，形成光斑，影响发光均匀度[29]。芯片在工作时放热剧烈，荧光粉和树脂紧密贴合在芯片周围，受热易发生老化，光衰大，将影响了纳米晶白光LED的使用寿命。

为了解决上述白光LED存在的问题，我们通过将$CuInS_2$纳米晶荧光粉和高聚物(PMMA)混合制得黄色的光转换膜[30]，该光转换膜的制备中不涉及固化的步骤。然后将光转换膜覆在蓝光LED芯片上，之间隔开一定距离组合成Remote型白光LED。蓝光LED发出的一部分蓝光激发光转化膜中的荧光粉发射出黄光，黄光与剩余的蓝光复合形成白光。黄色$CuInS_2$纳米晶荧光粉的颗粒很小，容易和封装材料混合均匀，从而提高了发光的均匀度。另一方面，光转换膜和蓝光LED芯片之间被空气隔开，芯片在工作过程中释放的热对光转换膜的影响将极大地降低，因

此可以延长白光LED的使用寿命，增加其稳定性。

5. 当前国内外研究水平

半导体纳米晶是新兴的颜色可调的光转换材料，在白光LED中的应用得到了人们的广泛关注，包括美国麻省理工学院、新加坡南洋理工大学、韩国亚洲大学、上海交通大学等单位都在研究基于纳米晶的白光LED的应用，取得了很多进展：

国内外同类研究水平概述	研究小组	纳米晶种类	传统荧光粉	显色指数	流明效率	色温
	2007年 Demir等[31]	CdSe/ZnS 纳米晶	无	14.69-71.07		2692 K-11171 K
	2007年 Jang等[14]	CdSe 纳米晶	黄绿色荧光粉 $Sr_3SiO_5:Ce^{3+}$, Li^+	90.1	14 lm/W	8864 K
	2008年 Ziegler等[32]	InP/ZnS 纳米晶	绿色荧光粉 $Sr_{0.94}Al_2O_4:Eu_{0.06}$ 和黄色荧光粉 YAG: Ce	86	10-20 lm/W	3200 K-6500 K
	2009年 Jeon等[20]	CdSe/ZnSe 纳米晶	黄绿色荧光粉 $Sr_3SiO_5:Ce^{3+}$, Li^+	85	26.8 lm/W	6140 K
	2010年 Woo等[33]	CdSe/CdS/ZnS 纳米晶	绿色荧光粉 $Sr_2SiO_4:Eu$	83.2	65.86 lm/W	
	2010年 Kim等[34]	绿色 CdSe//ZnS/CdSZnS 纳米晶和红色 CdSe/CdS/ZnS/CdSZnS 纳米晶	无		41 lm/W	
	2012年 李万万等[24]	CdS:Cu/ZnS 纳米晶	黄色荧光粉 YAG: Ce	90	40 lm/W	
	2012年 Yang等[21]	$CuInS_2$ 纳米晶	黄色荧光粉 YAG: Ce	72-75	63.4 lm/W	4447 K-5380 K
本作品		$CuInS_2$ 纳米晶	黄色荧光粉 YAG: Ce 和绿色荧光粉 $Sr_2SiO_4:Eu$	**93.1**	**45-60 lm/W**	**3000 K-11000 K**

目前纳米晶LED的应用受限与材料的毒性和稳定性。本作品所发展的$CuInS_2$纳米晶荧光粉具有以下特点与优势：半峰宽较大，可覆盖整个白光区域；可被LED芯片的蓝光所激发；斯托克斯位移大，自吸收小；成本低、易量产。国际上对这一材料在白光LED应用的研究刚刚起步，最近两年才有所报道，2012年，韩国弘益大学的Yang等人利用$CuInS_2$纳米晶制备出白光LED，然而其显色指数只有

75，不能满足室内照明的基本要求。本作品所制备的$CuInS_2$基纳米晶荧光粉绝对荧光量子产率高于75%，利用$CuInS_2$红色荧光粉制备的白光LED器件显色指数达93，效率为45-60 lm/W，色温在3000-11000K之间可调是目前这类材料的最好水平。此外，所制备的$CuInS_2$纳米晶的光转换膜以及Remote型白光LED，具有透光性好、色散小等优势，目前还未见报道。

6. 原型器件制备和性能测试

6.1 纳米晶荧光粉材料的合成

6.1.1 实验用品

试剂：碘化亚铜（Copper Iodide）、十二烷基硫醇（Dodecanethiol）、醋酸铟（Indium Acetate）、油酸（Oleic Acid）、醋酸锌（Zinc Acetate）、十八烯（Octadecene）、油胺（Oleylamine）、甲苯（Methylbenzene）、氯仿（Chloroform）、丙酮（Acetone）、无水甲醇（Methanol）硅胶OE6551A B、YAG黄色荧光粉、G2762 绿色荧光粉、聚甲基丙烯酸甲酯（PMMA）

实验设备：250 mL三口烧瓶、100 mL三口烧瓶、磁力搅拌台、氮气保护反应系统、加热套、注射器、荧光光谱仪、蓝光LED芯片、变压器

6.1.2 红色$CuInS_2$纳米晶荧光粉的合成

将碘化亚铜、醋酸铟、十二烷基硫醇、十八烯、油酸加入到100 mL三口烧瓶中混合，在氮气保护下加热到220 ℃，恒温反应1小时，得到$CuInS_2$纳米晶反应源。将醋酸锌、油胺、十八烯混合，混合溶液在氮气保护下升温到120 ℃，至浑浊溶液变清澈，制备得到锌源；在220 ℃下将上述锌源分次注入到$CuInS_2$纳米晶反应源中进行反应。

将反应得到的胶体溶液通过离心分离进行清洗，得到的纳米晶荧光材料，在50 ℃下真空干燥1 h得到粉末状产物，将粉末研磨保存待用。

6.1.3 黄色 $CuInS_2$ 纳米晶荧光粉的合成

采用与合成红色$CuInS_2$纳米晶荧光粉相似的方法可合成黄色$CuInS_2$纳米晶荧光粉，所不同是需用相同锌源对纳米晶反应源进行重复包覆。

6.2 白光 LED 及光转换膜原型器件的制备

6.2.1 双色混合型白光LED原型器件的制备

硅胶OE6551A、OE6551B与YAG荧光粉配制得到封装材料，将其移入5 mL针筒中，倒入的时候不可产生气泡；给针筒安装进气管，对进气管施加压力，使得针筒中的复合封装胶缓慢滴进贴片型LED杯碗中心的凹槽内，直至复合封装胶在杯碗中呈平杯状态（与凹槽口平齐），得到固化前的LED整体器件；整体器件放入干燥箱中，在120℃下烘烤3h，实现所述非稀土纳米晶荧光粉在白光LED中的应用，所述LED为贴片型LED。大功率型白光LED器件与贴片型操作基本一致，但多一步外封的过程。

6.2.2 三色混合型白光LED原型器件的制备

三色荧光粉（$CuInS_2$纳米晶荧光粉、YAG荧光粉和G2762绿色荧光粉）白光LED制备过程与双色荧光粉白光LED步骤相同，在复合封装胶中加入一定量的型号为G2762绿色荧光粉即可。

6.2.3 纳米晶荧光粉光转换膜原型器件的制备

将8 g的PMMA溶解在80 mL的$CHCl_3$中，制得透明的PMMA胶水；然后称取0.5 g的558 nm的$CuInS_2$纳米晶溶解在10 mL $CHCl_3$中，配得黄色的溶有荧光粉的溶液；称取0.01 g 610 nm的$CuInS_2$纳米晶溶解在10 mL $CHCl_3$中，配得红色的溶有荧光粉的溶液。按V(PMMA胶水):V(荧光粉溶液)=2:1的比例配置混合溶液，将所配的混合溶液均匀分散到培养皿中，待$CHCl_3$挥发后便制得所需的光转换膜。

6.3 白光 LED 与光转换膜原型器件的性能

6.3.1 荧光粉的光谱性质表征

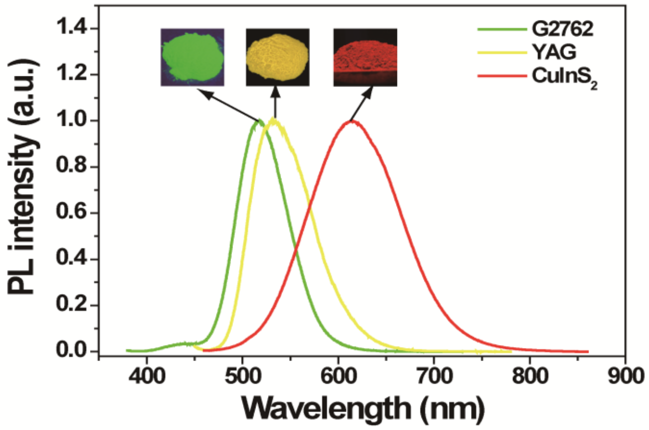


图1：YAG黄色荧光粉、G2762绿色荧光粉和红色CuInS$_2$纳米晶荧光粉的荧光光谱图；

图1给出黄色YAG荧光粉、G2762绿色荧光粉和红色CuInS$_2$纳米晶荧光粉的荧光光谱图以及紫外灯下发光照片图，从图中可以看出，红色CuInS$_2$纳米晶荧光粉的荧光光谱最大发射峰的位置在613 nm处，YAG荧光粉的最大发射峰的位置在540 nm处；G2762荧光粉的最大发射峰的位置在520 nm处；红色CuInS$_2$纳米晶荧光粉的半峰宽较大，用于白光LED能明显改善白光LED显色性不高的问题。

6.3.2 双色混合型白光LED原型器件和性能

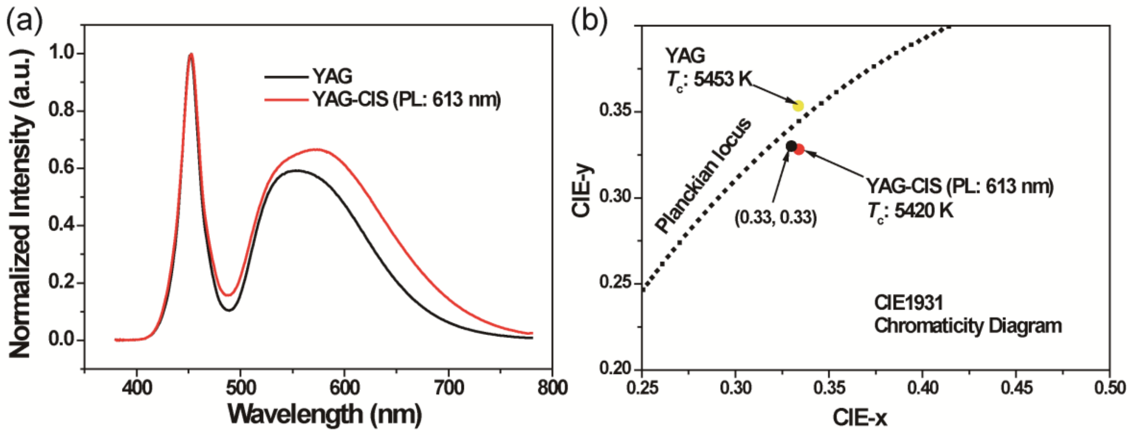


图2(a)：YAG荧光粉白光LED和红色CuInS$_2$纳米晶荧光粉与YAG荧光粉混合型白光LED的光谱曲线；(b)：两颗白光LED在色坐标中的位置；

图2(a)中的红色光谱是加了红色CuInS$_2$纳米晶荧光粉后的光谱曲线，可以看出该曲线和没有加红色CuInS$_2$纳米晶的YAG荧光粉制得的白光LED光谱相比波长范围变宽，覆盖的波长范围明显增长，从(b)中则可以明显看出制得的LED色

坐标更加接近标准白光色坐标(0.33,0.33)。

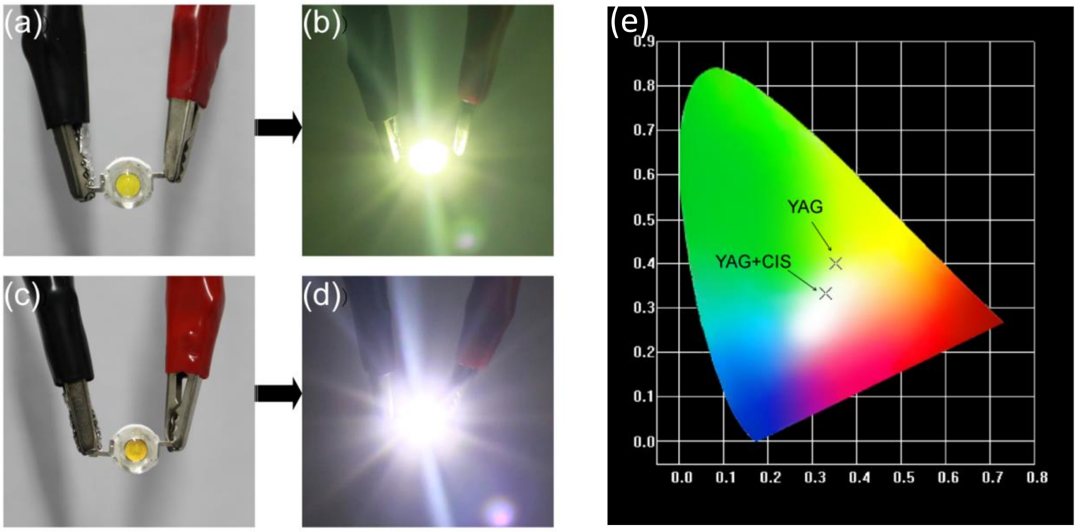


图3 (a), (b)：基于YAG荧光粉的白光LED实物和发光效果图
(c), (d)：基于YAG和红色$CuInS_2$纳米晶混合型白光LED实物和发光效果图；
(e)：两颗LED在彩色色坐标中的位置对比；

从图3中可以明显看出，加了红色$CuInS_2$纳米晶荧光粉后，发出的白光效果更好，亮度更亮；在彩色色坐标中两颗大功率白光LED的位置也明显说明了添加了红色$CuInS_2$纳米晶的白光LED在色坐标中的位置向正白光区域偏移。

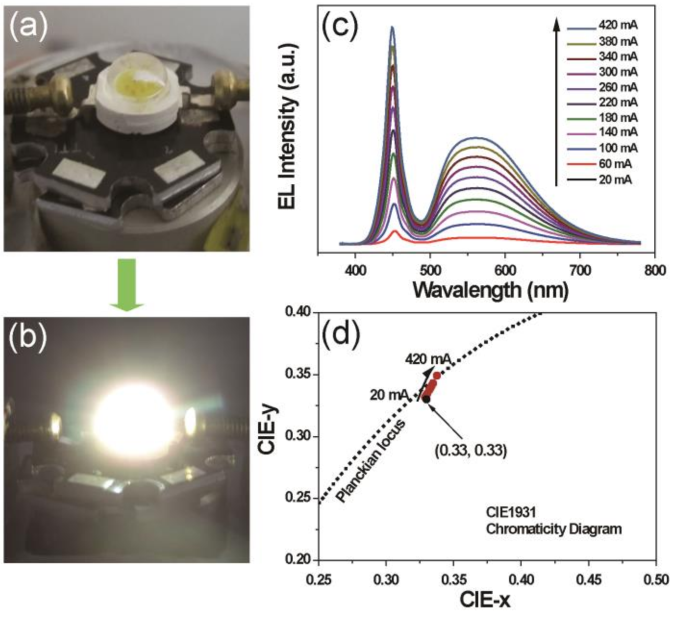


图4 (a), (b)：该白光LED的实物和发光效果图；
(c)：该白光LED在20 mA到420 mA不同电流下的发光光谱曲线；
(d)：不同电流下该白光LED的色坐标位置变化；

如图4(a)和(b)所示由YAG荧光粉和红色$CuInS_2$纳米晶荧光粉混合制得的大

功率白光LED在150 mA电流下发出很亮的白光。如图4(c)和(d)所示，在白光LED的发光光谱中从20 mA到420 mA的电流变化下呈现出一个460 nm的发射带。从图中可以看出在380 mA电流下白光LED的色坐标是(0.3239, 0.3324)，它的值在不同的电流下呈现出的变化很小，表明白光LED发出的光具有很好的稳定性。相比基于YAG荧光粉的白光LED 66.8的显色指数，基于$CuInS_2$纳米晶荧光粉和YAG荧光粉混合白光LED 显色指数可提高到76。尽管白光LED的显色指数得到了改善,但显色指数高于90的白光LED很少有报道，因为商业化的红色荧光粉如Y_2O_3: Eu^{3+}的发射波长通常低于630 nm,这使得它很难改善深红区域的显色性。

6. 3. 3 三色混合型白光LED原型器件的性能

基于YAG荧光粉和红色$CuInS_2$纳米晶荧光粉混合制得的白光LED虽然已经实现了显色指数的明显提升，但显色指数没有突破90，所以在YAG和$CuInS_2$纳米晶荧光粉混合的基础上，我们又引入了商业化的G2762绿色荧光粉，希望通过加入绿色荧光粉使得白光LED具有更优异的显色性。

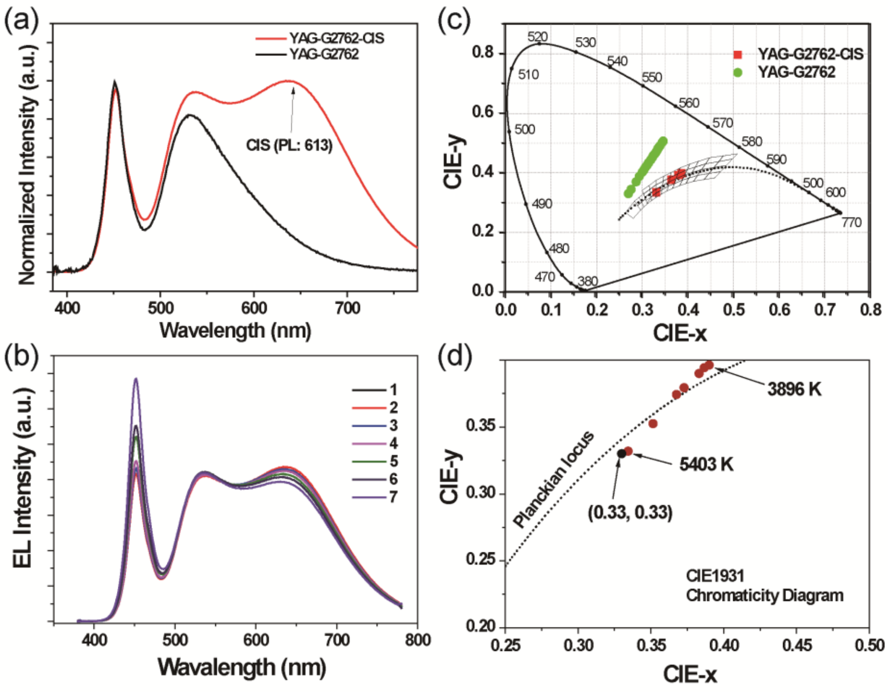


图5(a)：YAG与G2762双色混合型白光LED和加了$CuInS_2$纳米晶荧光粉的三色混合型白光LED发光光谱曲线对比；(b)：在G2762:YAG:$CuInS_2$ =12: 5: 1的比例下制得的几颗白光LED之间的平行对比；(c), (d)：该比例下的白光LED色坐标的位置；

图5(a)中加了$CuInS_2$纳米晶荧光粉的三色混合型白光LED的波峰宽度明显增长，图5(a)中的红色曲线在610 nm附近的出现一个波峰，550 nm附近出现另外一

个波峰，符合红色$CuInS_2$纳米晶荧光粉和YAG黄色荧光粉的发射峰。(c)中加了$CuInS_2$纳米晶荧光粉的三色混合型白光LED在色坐标中的曲线基本和黑体辐射线重合，该方案得到的贴片型白光LED显色指数达到了90以上，而且从(d)可以看出色温在5403 K的LED色坐标很接近于标准白光色坐标(0.33,0.33)。

表1：G2762:YAG:$CuInS_2$ =12:5:1时的几颗贴片型白光LED的数据

Samples	Partition	L_E (lm/W)	x	y	T_c(K)	R_a
1	d4-2	45.31	0.3867	0.3943	3962	91.5
2	d4-1	45.11	0.3831	0.39	4024	91.7
3	d5-2	45.5	0.3728	0.3794	4231	91.9
4	d5-2	45.37	0.3676	0.3743	4353	91.9
5	c6-2	44.97	0.3515	0.3525	4764	93.1
6		64.35	0.2794	0.2729	11304	90

从表1可以看出在不同色温下显色指数都达到了90以上；光效达到了45 lm/W；从色坐标中可以看出这几颗LED都属于品质很好的正白光LED。

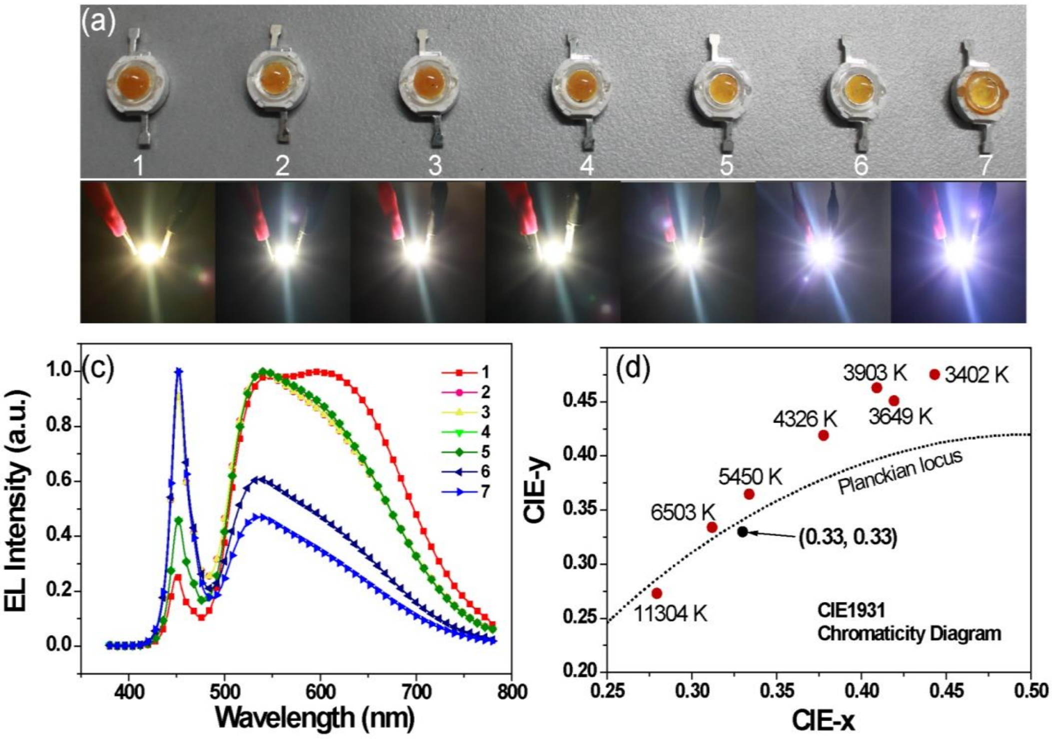


图6 (a), (b)：G2762:YAG:$CuInS_2$ =6:4:1的比例下制得的7颗大功率LED实物和发光效果图；(c)：每颗LED的发光光谱曲线；(d)：7颗LED的色坐标位置和色温变化；

不同领域和不同场合对白光LED的色温有不同的要求，我们通过改变点胶量实现了三色混合型大功率白光LED色温调控。如图6(a)所示从左到右点胶量逐渐减少，颜色逐渐变浅。图6(b)是其相应的白光LED发光效果图，从图中可以看出白光LED发光呈现冷白到暖白的递变趋势；(c)图给出相应的电致发光光谱图，从图中可以明显看到红色区域的增加。此红色区域来自于$CuInS_2$纳米晶荧光粉受到蓝光LED激发之后产生的红光。从(d)中可以看出该方案能得到不同色温下发光效果很好的白光LED，可覆盖整个白光区域，例如色温在3800 K以下的暖白光类型、3800 K到6500 K范围内的正白光类型、6500 K以上的冷白光类型，而且在色坐标中的位置离黑体辐射线都很近，白光质量很高。能够满足白光LED在背光源、照明、电子设备、显示屏、汽车等不同领域对色温的要求。

6. 3. 4 光转换膜的性能

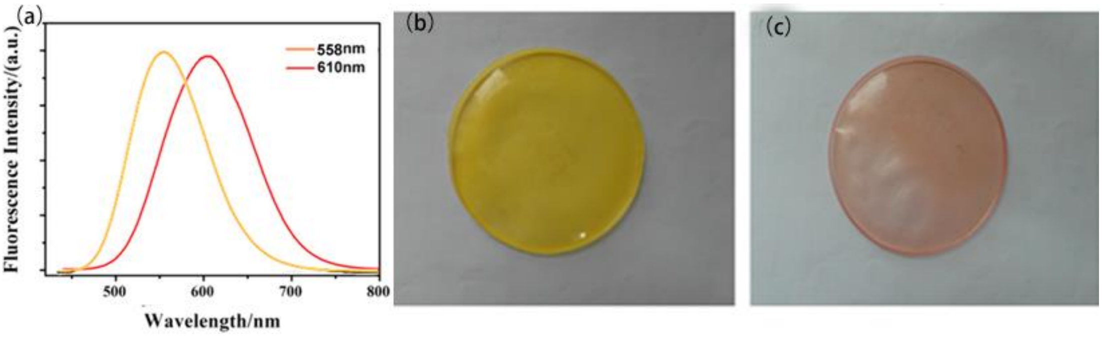


图 7 (a)分别是 558nm 和 610nm $CuInS_2$ 纳米晶的荧光发射光谱；
(b)是由 558nm $CuInS_2$ 纳米晶和 PMMA 复合得的黄色光转换膜；
(c)是由 610nm $CuInS_2$ 纳米晶和 PMMA 复合得的红色光转换膜。

从波谱表征中可以看出，黄色$CuInS_2$纳米晶荧光粉的荧光发射峰λ_{em}=558 nm，红色$CuInS_2$纳米晶荧光粉的荧光发射峰λ_{em}=610 nm。而且红色$CuInS_2$纳米晶的荧光发射峰的半峰宽明显比黄色$CuInS_2$纳米晶大，因而能够通过叠加红色光转换膜的方法来提高白光LED的显色指数。

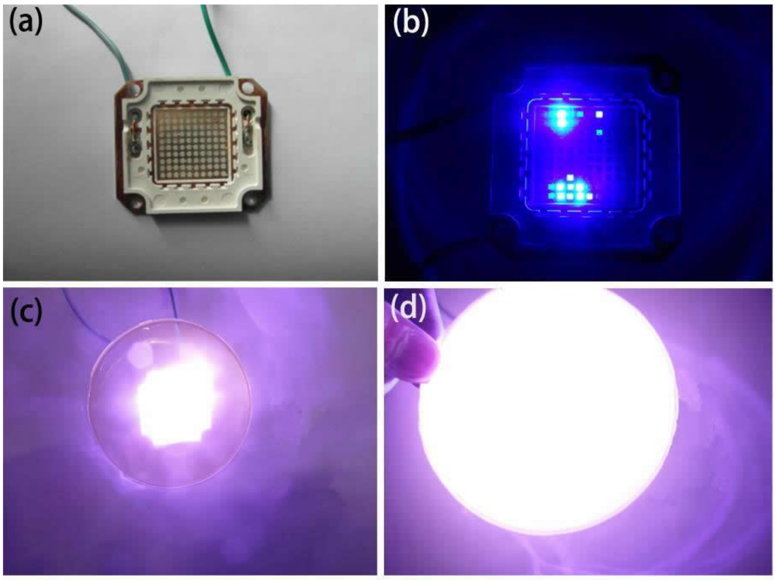


图 8　(a)是许多蓝光 LED 芯片组成的大功率蓝光 LED；

(b)是大功率蓝光 LED 的发光图片；

(c)是单独的黄色光转换膜在 LED 近距离照射下的发光图片；

(d)是单独的黄色光转换膜在 LED 远距离照射下的发光图片。

在蓝光LED的近距离照射下，光转换膜发白光的区域仅限于中心区域，将光转换膜与蓝光LED的距离稍微增大，发出的白光效果与前者基本相同，但光转换膜发白光面积增大，从而提高了蓝光的利用率和转换率。蓝光LED在工作过程中会不断向周围释放热量，对光转换膜有不利影响。光转换膜是由$CuInS_2$纳米晶和PMMA复合制成的，长时间处于热环境中，$CuInS_2$纳米晶的荧光量子产率降低，发光质量降低；PMMA的机械性能、透光性以及耐老化性能也都会受到影响。因此，将光转换膜应用到Remote白光LED中，能够实现散热效果与发光效果的协调。

7．技术分析与应用前景

7.1 白光 LED 的技术分析与应用前景

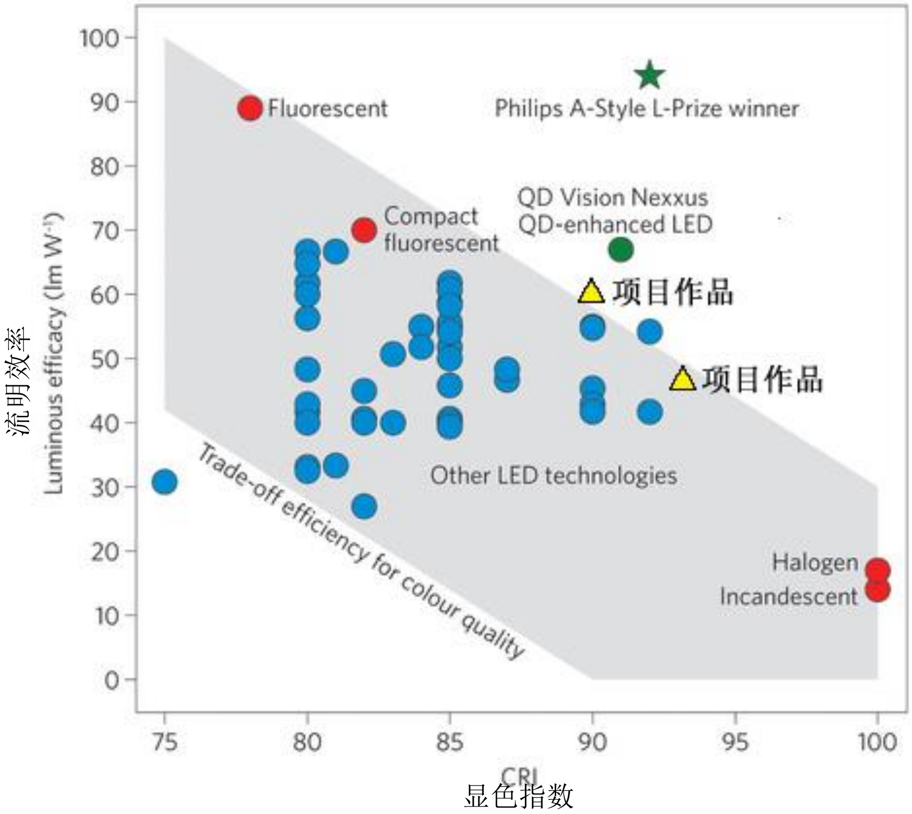


图9 项目所制备纳米晶白光LED性能与文献中现有白光照明技术参数的对比，黄色三角形所在位置为本项目数据，数据对比来自Nature Photonics, 2013, 7, 13-23综述。

本作品制备出发光波长为613 nm的红色$CuInS_2$纳米晶荧光粉，然后将红色$CuInS_2$纳米晶荧光粉、黄色YAG荧光粉和G2762绿色荧光粉混合，制得的贴片型和大功率型白光LED显色指数超过90，最高流明效率达到60 lm/W，色温在3000-11000 K之间可调，与商品化的LED以及国外公司相比显色指数和流明效率都处于先进水平(参见图9)，具有很大的技术潜力和发展前景。

LED作为一种新型固态照明光源，广泛应用于室内照明、景观照明、显示屏等照明显示领域。全球LED市场规模庞大，2011年，我国LED行业总产值增长至1540亿元。无论从产量还是产值，LED产业发展迅速。资料显示，未来景观照明和通用照明的LED市场增长速度更快。资料显示，2010年已增长到8.75亿美元，未来年增长率将达52.3%。其中高显色指数白光LED在照明市场中占据重要位置，且随着时间的推移，其所占市场比例也将逐年增大。本作品中的白光LED，具有

高显色指数、色温白光的优点，可提供更加优异的照明效果。此外，本作品中所使用的纳米晶荧光粉具有自主知识产权、成本低廉，未来有望突破国外专利壁垒。

7.2 光转换膜技术分析与应用前景

7.2.1 光转换膜应用于Remote白光LED

利用传统稀土荧光粉制成的光转换膜由于荧光粉的颗粒大、分散性差，较大的色散损失导致光转换膜的透光性差、光效低，且力学性能难以达到应用水平。本作品制备的纳米晶/聚合物复合光转换膜，由于纳米晶尺寸小、单分散性好，将其与PMMA复合，可以得到透明性好、光转换效率高且具有良好力学性能的光转换膜，将其应用于Remote结构LED器件中，可有效提高LED器件的寿命和光效。同时，对光转换膜中纳米晶发光波长进行调控，使其可以在多种照明和显示领域中得到应用。

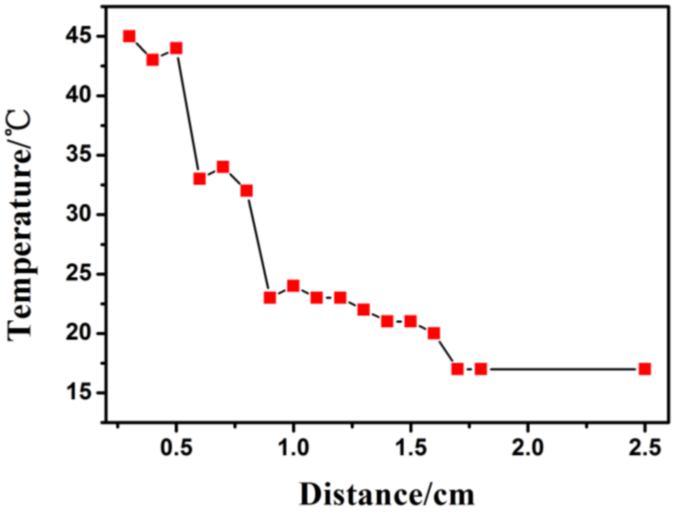


图10 黄色光转换膜在工作过程中温度随光转换膜和蓝光LED间距的变化，工作电压15 V，工作时间为3 min，室温17 ℃。

从图10中光转换膜的工作温度随光转换膜和蓝光LED间距的变化曲线可以看出，适当的增大光转换膜和蓝光LED的距离可以很好的降低在工作过程中光转换膜的温度变化，当光转换膜和蓝光LED的距离小于0.8 cm时，工作3 min后，光转换膜的温度就升高到了30 ℃以上，当距离小于0.5 cm时，工作3 min后，光转换膜的温度就升高到了40 ℃以上，而当距离大于0.9 cm时，光转换膜的温度在25 ℃以下。所以，将光转换膜与蓝光LED隔开一定的距离，一方面可以提高蓝光的利用率，另一方面还可以减少蓝光LED工作时释放的热量对光转换膜的影响，

从而提高Remote白光LED的稳定性和使用寿命。

7.2.2 光转换膜应用于通用照明领域

光转换膜作为一种多功能发光原件，正受到人们的日益关注，但目前对其进行的研发工作不系统，所制备的照明器件也不成熟，产品化应用少，所占市场比例较小。本文所制备光转换膜发光波段可控、颜色可调，使用的$CuInS_2$纳米晶荧光粉与PMMA能均匀混合，成膜过程工艺简单，在不同照明领域的应用中有巨大的发展潜力。本作品在获得一系列不同发光颜色的纳米晶/复合物光转换膜后，对其在通用照明领域的应用进行了初步探索，设计出一种色温可调照明灯具，通过更换光转换膜，可实现照明光色温的调节，达到“一灯多用”的效果。其创新点是在同一灯具中可应用不同颜色的光转换膜，通过简单操作达到改变光色、光强的效果，同时具有实用价值和观赏价值。本作品制备的光转换膜还可进一步研发类似的玩具、小饰品等，具有广阔的应用前景和市场价值。

7.2.3 光转换膜应用于农用补光

室内许多观赏性植物太阳光并不能完全满足植物光合作用的需求，这时，可以通过一个基于蓝光LED的光转换膜系统来达到额外补光的目的，通过蓝光激发产生的红橙光和剩余的蓝光都是植物光合作用所需的组分，此外通过改变光转换膜的厚度可以调节透过光中蓝光所占比例，以此可满足植物不同生长过程中对光的需求。同时，室外农用补光膜是通过将太阳光线中的紫外光和对农作物光合作用没有效果的绿光转换为可供植物吸收利用的红橙光，从而提高农作物的光合作用，增加农作物产量。

综上所述，光转换膜可应用范围广泛，除可应用于上述领域，还可应用于诸如LED背光源、广告展示等方面，且光转换膜成膜工艺简单，成本低廉，具有巨大的市场潜力和广阔的应用前景。

参考文献

[1] http://www.bjkw.gov.cn/n1143/n1240/n1375/index.html.

[2] Humphreys C J. Solid-State Lighting[J]. MRS Bulletin, 2008, 33: 459-470.

[3] Schubert E F, Kim J K. Solid-state light sources getting smart[J]. Science 2005, 308(5726): 1274–1278 .

[4] Erdem T, Demir H V. Semiconductor Nanocrystals as Rear-earth Alternatives[J]. Nat. Photonics, 2011, 5(126).

[5] Qian L, Zheng Y, Xue J G, Holloway H. Stable and efficient quantum-dot light-emitting diodes based on solution-processed multilayer structures[J]. Nat. Photonics, 2011, 5: 543-548.

[6] Kim T H, Cho K S, Lee E K, Lee S J, Chae J, Kim J W, Kim D H, Kwon J Y, Amaratunga G, Lee S Y, Choi B L, Kuk Y, Kim J M, Kim K. Full-colour quantum dot displays fabricated by transfer printing[J]. Nat. Photonics, 2011, 5: 176-182.

[7] Shirasaki Y, Supran G J, Bawendi M G, Bulovic V. Emergency of Colloidal Quantum-Dot Light-Emitting Technologies[J]. Nat. Photonics, 2013, 7: 13-23.

[8] Bourzac K. Quantum dots go on display-Adoption by TV makers could expand the market for light-emitting nanocrystals[J]. Nature, 2013,493: 283.

[9] 张其乐，张乐，韩朋德，陈雁，杨浩，王丽熙. 白光 LED 用光转换无机荧光粉[J]. 化学进展，2011，23: 1108-1122.

[10] Dai Q Q, Duty C E, Hu M Z. Semiconductor-nanocrystals-based white light-emitting diodes[J]. 2010, Small, 6(15): 1577–1588.

[11] Höppe H A. Recent developments in the field of inorganic phosphors[J]. Angew. Chem. Int. Ed, 2009, 48(20): 3572–3582.

[12] Lin C C, Liu R S. Advances in phosphors for light-emitting diodes[J]. J. Phys. Chem. Lett, 2011, 2(11): 1268–1277.

[13] Schreuder M A, Gosnell J D, Smith N J, Warnement M R, Weiss S M, Rosenthal S J. Encapsulated white-light CdSe nanocrystals as nanophosphors for solid-state lighting[J]. J. Mater. Chem, 2008, 18(9): 970–975.

[14] Jang H S, Yang H, Kim S W, Han J Y, Lee S G, Jeon D Y, White light-emitting

diodes with excellent color rendering based on organically capped CdSe quantum dots and Sr_3SiO_5:Ce^{3+}, Li^+ phosphors[J]. Adv. Mater, 2008, 20(14): 2696–2702.

[15] Nizamoglu S, Mutlugun E, Özel T, Demir H V, Sapra S, Gaponik N, Eychmüeller A. Dual-color emitting quantum-dot-quantum-well CdSe-ZnS heteronanocrystals hybridized on InGaN/GaN light emitting diodes for high-quality white light generation[J].2008, Appl. Phys. Lett, 92(11): 113-110.

[16] Nizamoglu S, Erdem T, Sun X W, Demir H V. Warm-white light-emitting diodes integrated with colloidal quantum dots for high luminous efficacy and color rendering[J]. Opt. Lett, 2010, 35(20): 3372–3374.

[17] Nizamoglu S, Zengin G, Demir H V. Color-converting combinations of nanocrystal emitters for warmwhitelight generation with high color rendering index[J]. Appl. Phys. Lett, 2008, 92(3): 102-104.

[18] Shen C Y, Li K, Hou Q L, Feng H J, Dong X Y. White LED Based on YAG: Ce,Gd Phosphor and CdSe-ZnS Core/Shell Quantum Dots[J]. IEEE Photon. Technol. Lett, 2010, 22(12): 884–886.

[19] Kim K, Woo J Y, Jeong S, Han C S. Photoenhancement of a quantum dot nanocomposite via UV annealing and its application to white LEDs[J]. Adv. Mater, 2011, 23(7): 911–914.

[20] Jang H S, Kwon B H, Yang H, Jeon D Y. Bright three-band white light generated from CdSe/ZnSequantum dot-assisted Sr_3SiO_5:Ce^{3+},Li^+-based white light-emitting diode with high color rendering index[J]. Appl. Phys. Lett, 2009, 95(16): 16-19.

[21] Wang X B, Yan X S, Li W W, Sun K. Doped quantum dots for white-light-emitting diodes without reabsorption of multiphase phosphors[J]. Adv. Mater, 2012, 24(20): 2742–2747.

[22] Zhong H Z, Bai Z L, Zou B S. Tuning the luminescence properties of colloidal I–III–VI semiconductor nanocrystals for optoelectronics and biotechnology applications[J]. J. Phys. Chem. Lett, 2012, 3(21): 3167–3175.

[23] Chung W, Jung H, Lee C H, Kim S H. Fabrication of high color rendering index white LED using Cd free wavelength tunable Zn doped $CuInS_2$ nanocrystals[J]. Opt. Express, 2012, 20(22): 25071–25076.

[24] Song W S, Yang H. Efficient white-light-emitting diodes fabricated from highly fluorescent copper indium sulfide core/shell quantum dots[J]. Chem. Mater, 2012, 24(10): 1961–1967.

[25] Kim H, Jang H S, Kwon B H, Suh M, Kim Y, Cheong S H, Jeon D Y. In situ synthesis of thiol- capped $CuInS_2$-ZnS quantum dots embedded in silica powder by sequential ligand-exchange and silanization[J]. Electrochem. Solid-State Lett, 2012, 15(2): 16–18.

[26] Chen B K, Zhou Q C, Li J F, Zhang F, Liu R B, Zhong H Z, Zou B S. Red emissive $CuInS_2$-based nanocrystals: a potential phosphor for warm white light-emitting diodes[J]. Opt. Express, 2013, 21(8): 10105-10110.

[27] Chen B K, Zhong H Z, Wang M X, Liu R B, Zou B S. High Efficiency and High Color Rendering White Light-Emitting Diodes with Tunable Color Temperature using $CuInS_2$ Based Nanocrystals[J]. Nanoscale, 2013, 5: 3514-3519.

[28] Chen B K, Zhong H Z, Zhang W Q, Tan Z A, Li Y F, Yu C L, Zhai T Y, Bando Y, Yang S Y, Zou B S. Highly emissive and color-tunable $CuInS_2$-based colloidal semiconductor nanocrystals: offstoichiometry effects and improved electroluminescence performance[J]. Adv. Funct. Mater, 2012, 22(10): 2081-2088.

[29] Pan C T, Chen M F, Cheng P J, Wang Y M, Tseng S D, Huang J C. Fabrication of gapless dual-curvature microlens as a diffuser for a LED package[J]. Sensors and Actuators Physical, 2009, 1(150):156-167.

[30] Kasuya R, Kawano A, Isobe T, Kuma H, Katano J. Characteristic optical properties of transparent color conversion film prepared from YAG:Ce^{3+} nanoparticles[J]. Appl. Phys. Lett, 2007, 91: 911-916.

[31] Nizamoglu S, Ozel T, Sari E. White light generation using CdSe/ZnS core–shell nanocrystals hybridized with InGaN/GaN light emitting diodes[J]. Nanotechnology, 2007, 18(6): 065709.

[32] Ziegler J, Xu S, Kucur E. Silica‐Coated InP/ZnS Nanocrystals as Converter Material in White LEDs[J]. Advanced Materials, 2008, 20(21): 4068-4073.

[33] Woo J Y, Kim K N, Jeong S. Thermal behavior of a quantum dot nanocomposite as a color converting material and its application to white LED[J]. Nanotechnology,

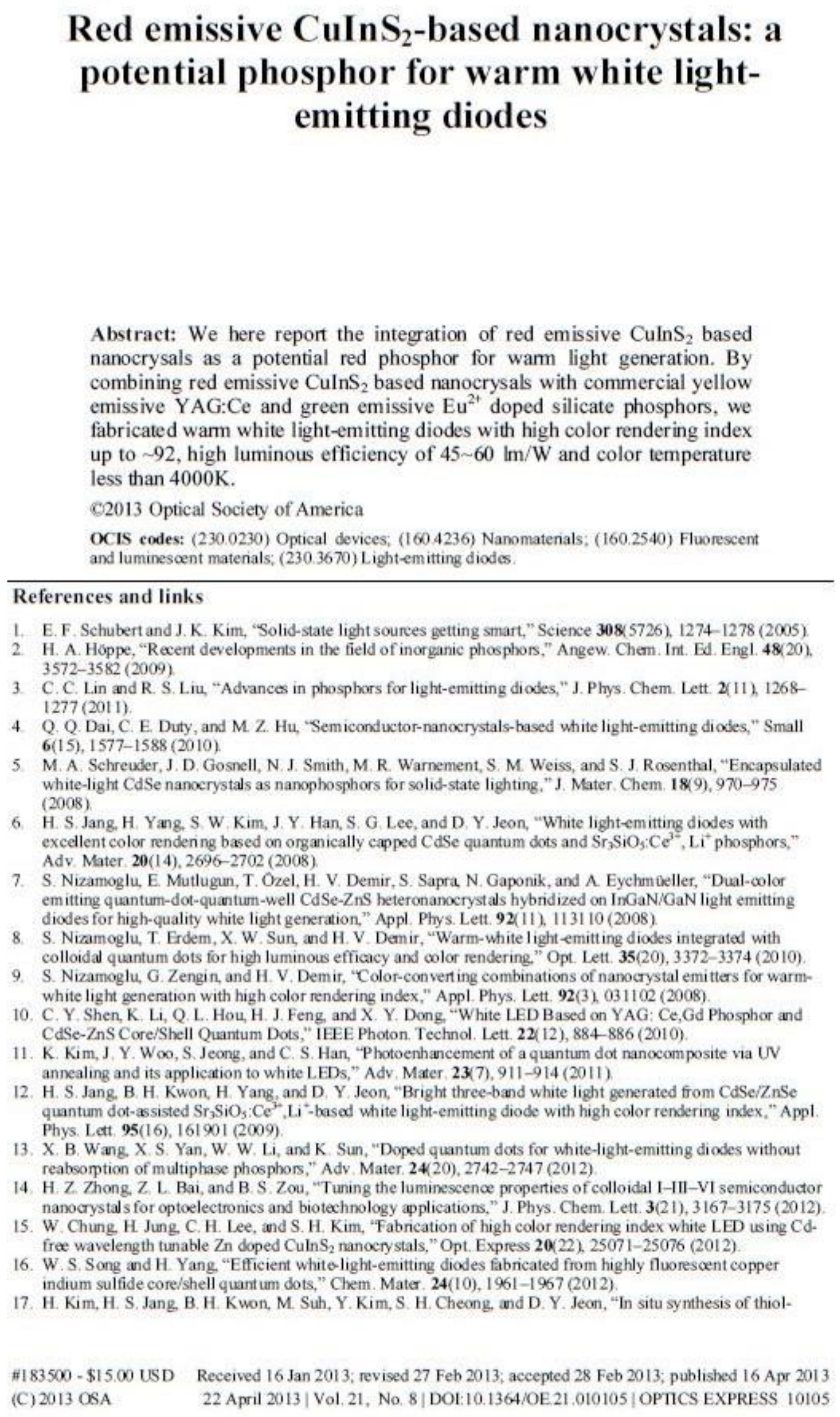
2010, 21(49): 495704.

[34] Jang E, Jun S, Jang H. White‐Light‐Emitting Diodes with Quantum Dot Color Converters for Display Backlights[J]. Advanced Materials, 2010, 22(28): 3076-3080.

附加材料清单

附加材料1：在美国光学期刊Optics Express发表的该作品相关论文文稿
附加材料2：专家推荐表

附加材料1：在美国光学期刊Optics Express发表的该作品相关论文文稿



Red emissive $CuInS_2$-based nanocrystals: a potential phosphor for warm white light-emitting diodes

Abstract: We here report the integration of red emissive $CuInS_2$ based nanocrysals as a potential red phosphor for warm light generation. By combining red emissive $CuInS_2$ based nanocrysals with commercial yellow emissive YAG:Ce and green emissive Eu^{2+} doped silicate phosphors, we fabricated warm white light-emitting diodes with high color rendering index up to ~92, high luminous efficiency of 45~60 lm/W and color temperature less than 4000K.

OCIS codes: (230.0230) Optical devices; (160.4236) Nanomaterials; (160.2540) Fluorescent and luminescent materials; (230.3670) Light-emitting diodes.

References and links

1. E. F. Schubert and J. K. Kim, "Solid-state light sources getting smart," Science **308**(5726), 1274–1278 (2005).
2. H. A. Höppe, "Recent developments in the field of inorganic phosphors," Angew. Chem. Int. Ed. Engl. **48**(20), 3572–3582 (2009).
3. C. C. Lin and R. S. Liu, "Advances in phosphors for light-emitting diodes," J. Phys. Chem. Lett. **2**(11), 1268–1277 (2011).
4. Q. Q. Dai, C. E. Duty, and M. Z. Hu, "Semiconductor-nanocrystals-based white light-emitting diodes," Small **6**(15), 1577–1588 (2010).
5. M. A. Schreuder, J. D. Gosnell, N. J. Smith, M. R. Warnement, S. M. Weiss, and S. J. Rosenthal, "Encapsulated white-light CdSe nanocrystals as nanophosphors for solid-state lighting," J. Mater. Chem. **18**(9), 970–975 (2008).
6. H. S. Jang, H. Yang, S. W. Kim, J. Y. Han, S. G. Lee, and D. Y. Jeon, "White light-emitting diodes with excellent color rendering based on organically capped CdSe quantum dots and $Sr_3SiO_5:Ce^{3+}$, Li^+ phosphors," Adv. Mater. **20**(14), 2696–2702 (2008).
7. S. Nizamoglu, E. Mutlugun, T. Özel, H. V. Demir, S. Sapra, N. Gaponik, and A. Eychmüeller, "Dual-color emitting quantum-dot-quantum-well CdSe-ZnS heteronanocrystals hybridized on InGaN/GaN light emitting diodes for high-quality white light generation," Appl. Phys. Lett. **92**(11), 113110 (2008).
8. S. Nizamoglu, T. Erdem, X. W. Sun, and H. V. Demir, "Warm-white light-emitting diodes integrated with colloidal quantum dots for high luminous efficacy and color rendering," Opt. Lett. **35**(20), 3372–3374 (2010).
9. S. Nizamoglu, G. Zengin, and H. V. Demir, "Color-converting combinations of nanocrystal emitters for warm-white light generation with high color rendering index," Appl. Phys. Lett. **92**(3), 031102 (2008).
10. C. Y. Shen, K. Li, Q. L. Hou, H. J. Feng, and X. Y. Dong, "White LED Based on YAG: Ce,Gd Phosphor and CdSe-ZnS Core/Shell Quantum Dots," IEEE Photon. Technol. Lett. **22**(12), 884–886 (2010).
11. K. Kim, J. Y. Woo, S. Jeong, and C. S. Han, "Photoenhancement of a quantum dot nanocomposite via UV annealing and its application to white LEDs," Adv. Mater. **23**(7), 911–914 (2011).
12. H. S. Jang, B. H. Kwon, H. Yang, and D. Y. Jeon, "Bright three-band white light generated from CdSe/ZnSe quantum dot-assisted $Sr_3SiO_5:Ce^{3+}$,Li^+-based white light-emitting diode with high color rendering index," Appl. Phys. Lett. **95**(16), 161901 (2009).
13. X. B. Wang, X. S. Yan, W. W. Li, and K. Sun, "Doped quantum dots for white-light-emitting diodes without reabsorption of multiphase phosphors," Adv. Mater. **24**(20), 2742–2747 (2012).
14. H. Z. Zhong, Z. L. Bai, and B. S. Zou, "Tuning the luminescence properties of colloidal I–III–VI semiconductor nanocrystals for optoelectronics and biotechnology applications," J. Phys. Chem. Lett. **3**(21), 3167–3175 (2012).
15. W. Chung, H. Jung, C. H. Lee, and S. H. Kim, "Fabrication of high color rendering index white LED using Cd-free wavelength tunable Zn doped $CuInS_2$ nanocrystals," Opt. Express **20**(22), 25071–25076 (2012).
16. W. S. Song and H. Yang, "Efficient white-light-emitting diodes fabricated from highly fluorescent copper indium sulfide core/shell quantum dots," Chem. Mater. **24**(10), 1961–1967 (2012).
17. H. Kim, H. S. Jang, B. H. Kwon, M. Suh, Y. Kim, S. H. Cheong, and D. Y. Jeon, "In situ synthesis of thiol-

#183500 - $15.00 USD Received 16 Jan 2013; revised 27 Feb 2013; accepted 28 Feb 2013; published 16 Apr 2013
(C) 2013 OSA 22 April 2013 | Vol. 21, No. 8 | DOI:10.1364/OE.21.010105 | OPTICS EXPRESS 10105

dotted line presents the color coordinates of WLEDs based on G2762 and YAG:Ce phosphors. It is obvious that all the color coordinates are out of the white light region and the color coordinates shifted to white light region with adding red emissive $CuInS_2$ NCs. Impressively, the WLEDs based on three phosphors have CIE color coordinates of (0.334-0.390, 0.332-0.396), CRI value of ~92 and luminous efficiencies of ~45 lm/W. By varying the amount of curing silicone resin, the devices exhibit tunable correlated color temperature along the Planckian locus from 3800 K to 5400 K.

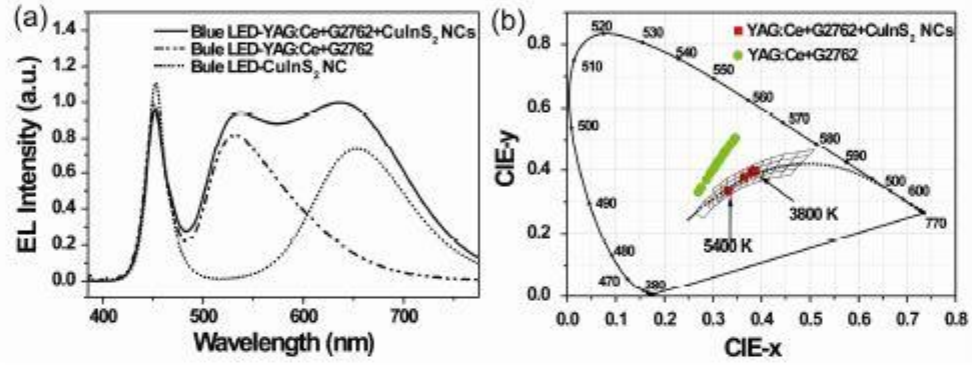


Fig. 3. (a) EL spectra of blue LED chip coated with G2762 and YAG:Ce phosphors, blue LED chip coated with $CuInS_2$ based NCs, and blue LED chip with a mixture of G2762, YAG:Ce phosphors and $CuInS_2$ based NCs. (b) CIE color coordinates of the WLED devices based on dual phosphors (G2762, YAG:Ce) and hybrid composites of three phosphors (G2762, YAG:Ce and $CuInS_2$ based NCs).

Table 2. The luminous efficiencies (L_E), CIE coordinates (x, y), color temperatures (T_c) and color rendering index (R_a) of the as-fabricated three-phosphors WLEDs with SMD type (operated at 20 mA) and high power type (operated at 350 mA).

Device	L_E (lm/W)	x	y	T_c (K)	R_a
SMD-1	45.1	0.390	0.396	3800	91.8
SMD-2	45.3	0.387	0.394	3962	91.5
SMD-3	45.1	0.383	0.390	4024	91.7
SMD-4	45.5	0.373	0.379	4231	91.9
SMD-5	45.4	0.368	0.374	4353	91.9
SMD-6	45.0	0.352	0.353	4764	93.1
SMD-7	45.4	0.334	0.332	5400	92.8
*HP-1	49.1	0.443	0.475	3402	79.4
*HP-2	60.3	0.419	0.451	3649	81.6

SMD: surface mounted devices; *HP: high power typed devices.

The indoor lighting requires high color rendering warm white light. The CCT of three-phosphors WLED devices was further tuned to generate warm light (< 4000 K). By increasing the concentration of phosphors in silicone resin, we fabricated high power type devices with tunable CCT from 3402 to 11304 K (see Table 2). As shown in Fig. 4(a), the color of the silicone resin shifted from light orange to deep orange-red with the increase of phosphors in silicone resin. Figure 4(b) shows the generated white lighting with CCT of 3402 K, 3649 K, 3903 K, 4326 K,5450 K, 6503 K and 11304 K. By visual observation, sample 7 and 6 show cool white light, sample 5, 4 and 3 show pure white light, sample 2 and 1 show warm white light. This change also correspond to the EL spectra measurements. As shown in Fig. 4(c), the red emission intensity around 620 nm greatly increased with $CuInS_2$ NCs adding. From Fig. 4(c), it is observed that all the devices have CIE color coordinates in the white light region along with the Planckian locus. It is worth to noted that the two devices with CIE coordinates of (0.2794, 0.2729), (0.312, 0.334) and CCTs of 3402, 3649 K generate high color rendering warm light with a CRI of ~80. In addition, the high power devices have luminous efficiency of 50~60 lm/W, which is acceptable for commercial applications.

A simple way to improve the color rendering index (CRI) value of commercial YAG:Ce based pc-WLEDs is to add red emissive phosphors [21]. The surface mounted devices (SMD) were fabricated by employing a blend of red emissive $CuInS_2$ based NCs and YAG:Ce phosphor with an thermally curable silicone resin (OE-6551AB, Dow Corning Co.). Figure 2(a) shows the EL spectrum of YAG:Ce based pc-WLEDs with (red line) and without (black line) $CuInS_2$ based NCs. Figure 2(b) depicts the different CIE color coordinates of the chromaticity diagram between the dual phosphor and the single phosphor based WLEDs. The color coordinate of the single phosphor based device locates at (0.334, 0.353), which is out of white light region. Obviously, by adding red emissive $CuInS_2$ NCs, the color coordinate of device based on dual phosphors moved to white light region (0.334, 0.328), which is quite close to pure white CIE color coordinates (0.333, 0.333). Table 1 summarized the parameters of surface mounted devices based on dual phosphors operated at 20 mA. The WLEDs based on dual phosphors exhibit improved CRI of ~82, which is much better than that of the single phosphor based WLEDs (CRI: R_a = 71). The luminous efficiency slightly decreased from ~110 lm/W to ~91 lm/W with adding $CuInS_2$ based NCs into silicone resin. This is a reasonable result for dual phosphor based WLEDs [21].

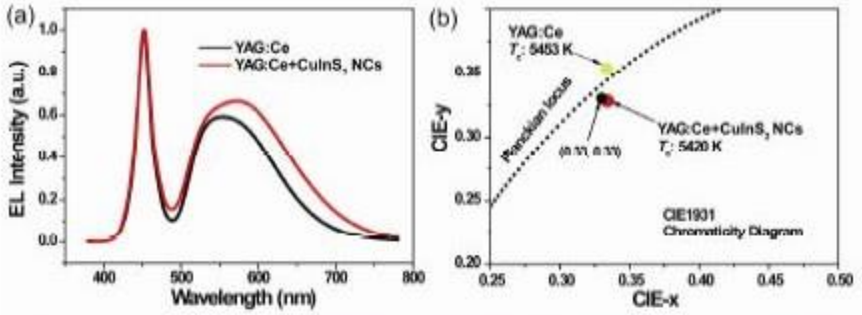


Fig. 2. (a) EL spectra of the as-fabricated surface mounted devices operated at a forward bias current of 350 mA using YAG:Ce (black line), YAG:Ce and red $CuInS_2$ NCs (red line). (b) CIE chromaticity diagram of the devices based on YAG: Ce phosphor with and without red $CuInS_2$ based NCs.

Table 1. The luminous efficiencies (L_E), CIE coordinates (x, y), color temperatures (T_c) and color rendering index (R_a) of the dual-phosphors surface mounted devices operated at 20 mA.

Samples	L_E (lm/W)	x	y	T_c (K)	R_a
YAG + $CuInS_2$ NCs	91.4	0.334	0.328	5420	81.9
YAG	106.9	0.334	0.353	5453	71.2

Although the incorporation of red emissive $CuInS_2$ based NCs into YAG:Ce based WLEDs obviously improved the CRI value of WLEDs, this strategy cannot generate warm white light with high CRI for indoor lighting. A combination of three phosphors was applied to improve the color rendering index and tune the correlated color temperature (CCT) for warm light generation. A green emissive Eu^{2+} doped silicate phosphor (G2762, PL spectrum was shown in Fig. 1(b)) was introduced. Table 2 summarized the parameters of three-phosphor based WLEDs with SMD type. The as fabricated SMD type WLEDs with a combination of green, yellow and red emissive phosphors (weight ratio of 12:5:1) exhibit excellent CRI up to ~92. A typical EL spectrum of three-phosphor based WLED with SMD type is shown in Fig. 3(a). It is observed that the EL spectrum has three obvious emission peaks at 455, 535 and 640 nm, corresponding to blue InGaN LED chip, G2762, and red emissive $CuInS_2$ based NCs respectively. We further studied the influence of red emissive $CuInS_2$ based NCs on the CIE color coordinates and color temperature of WLEDs. Figure 3(b) shows the CIE color coordinates of various devices using dual phosphors (G2762 and YAG:Ce) or three phosphors (G2762,YAG:Ce and red emissive $CuInS_2$ NCs). The green

#183500 - $15.00 USD Received 16 Jan 2013; revised 27 Feb 2013; accepted 28 Feb 2013; published 16 Apr 2013
(C) 2013 OSA 22 April 2013 | Vol. 21, No. 8 | DOI:10.1364/OE.21.010105 | OPTICS EXPRESS 10108

concentrations of phosphors in silicone resin for SMD and HP devices were 17.4% and 22% respectively.

3. Results and discussions

The red emissive $CuInS_2$ based NCs were synthesized through a colloidal solution method, which has been described in our previous report [20]. Figure 1(a) shows the absorption and photoluminescence (PL) spectra of typical red emissive $CuInS_2$ based NCs. The absolute PL quantum yield (QY) of red emissive $CuInS_2$ based NCs was determined to be ~75% using Quantaurus Tau QY measurement system. It is noted that the red emissive $CuInS_2$ based NCs can be efficiently excited by the blue chip (emission peak at 455 nm) due to their strong absorption in the wavelength region from UV to blue. The red emissive $CuInS_2$ based NCs have an emission peak at 614 nm and their emission spectrum extend to deep red region (>700 nm) with FWHM of ~113 nm. These properties enable them to be suitable red color converting materials for WLEDs. As shown in the TEM images in inset of Fig. 1(a), the red emissive $CuInS_2$ NCs have an average particle size of 5.4 nm. The green emissive Eu^{2+} doped silicate (G2762) and yellow emissive YAG:Ce phosphors are commercial products from Intematix corporation. Their emission spectra are depicted in Fig. 1(b). The emission spectra of these phosphors match well with the electroluminescence (EL) spectra of blue chips for white light generation. Especially, the red emissive $CuInS_2$ NCs can compensate the missing red and deep-red regions.

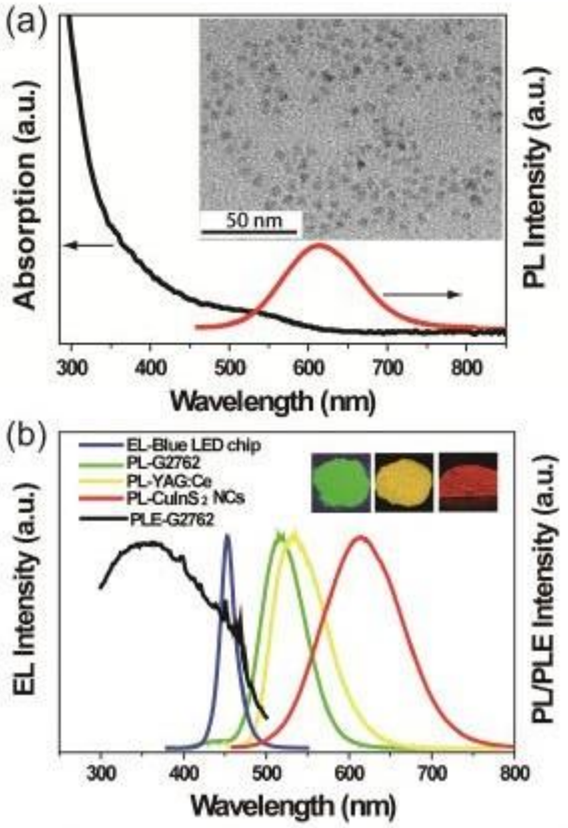


Fig. 1. (a) Absorption (black solid line), PL spectra (red solid line) excited at 450 nm and TEM image (inset) of typical red emissive $CuInS_2$ based NCs. (b) PL and PLE spectra of G2762, YAG:Ce phosphors and red emissive $CuInS_2$ based NCs excited at 450 nm, EL spectrum of blue LED chip (blue solid line); Inset: the corresponding picture of G2762, YAG:Ce phosphors and red emissive $CuInS_2$ NCs under UV radiation.

#183500 - $15.00 USD Received 16 Jan 2013; revised 27 Feb 2013; accepted 28 Feb 2013; published 16 Apr 2013

capped CuInS$_2$-ZnS quantum dots embedded in silica powder by sequential ligand-exchange and silanization," Electrochem. Solid-State Lett. **15**(2), K16–K18 (2012).
18. J. Ziegler, S. Xu, E. Kucur, F. Meister, M. Batentschuk, F. Gindele, and T. Nann, "Silica-coated InP/ZnS nanocrystals as converter material in white LEDs," Adv. Mater. **20**(21), 4068–4073 (2008).
19. S. Kim, T. Kim, M. Kang, S. K. Kwak, T. W. Yoo, L. S. Park, I. Yang, S. Hwang, J. E. Lee, S. K. Kim, and S. W. Kim, "Highly luminescent InP/GaP/ZnS nanocrystals and their application to white light-emitting diodes," J. Am. Chem. Soc. **134**(8), 3804–3809 (2012).
20. B. K. Chen, H. Z. Zhong, W. Q. Zhang, Z. A. Tan, Y. F. Li, C. L. Yu, T. Y. Zhai, Y. Bando, S. Y. Yang, and B. S. Zou, "Highly emissive and color-tunable CuInS$_2$-based colloidal semiconductor nanocrystals: off-stoichiometry effects and improved electroluminescence performance," Adv. Funct. Mater. **22**(10), 2081–2088 (2012).
21. R. J. Xie, Y. Q. Li, N. Hirosaki, and H. Yamamoto, *Nitride Phosphors and Solid State Lighting* (Taylor & Francis, Boca Raton, London, New York, 2011), Chap. 7.

1. Introduction

Among solid-state lighting technology, phosphor-converted white light-emitting diodes (pc-WLEDs) are excellent candidates to replace incandescent lamps for their merit of high energy conservation, long lifetime, high luminous efficiency as well as polarized emissions [1]. To generate warm light for general indoor lighting, red phosphors are very necessary [2,3]. Semiconductor nanocrystals (NCs) are emerging color tunable emissive light converters [4]. It has been demonstrated that the pc-WLED devices integrated with red emissive CdSe/ZnS, CdS:Cu/ZnS NCs show improved color rendering metric [5–13]. However, cadmium based NCs have limited future owing to the well-known toxicity. Recently, CuInS$_2$ and InP based NCs, are investigated as desirable low toxic alternatives [14–19]. Particularly, CuInS$_2$ based NCs exhibit very broad emissions spectra with full width at half maximum (FWHM) of 100-120 nm, large Stokes shifts of 200~300 meV and finely-tunable emissions [14]. These notable features provide great advantages to improve the color rending as well as tune the color temperature in WLEDs applications. In this work, we firstly demonstrated the applicability of red emissive CuInS$_2$ based NCs as a phosphor for high color rendering warm light generating.

2. Experimental section

CuInS$_2$ based NCs with emission peaks of 614 nm were prepared according to the method described in our previous work [20]. CuI (0.19 g, 1 mmol), In(OAc)$_3$ (1.16 g, 4 mmol) were mixed with dodecanethiol (DDT, 5 mL) and 1-octadecene (ODE, 25 mL) in a 100 mL three-necked flask. Then the reaction mixture was degassed under vacuum for 20 min at 120 °C. Oleic acid (OA, 2.5 mL) was added into the reaction flask, and the solution was continuously degassed for another 20 min under nitrogen flow. The solution was then heated to 220 °C to form a deep red colloidal solution. After that, DDT (5 mL) was injected into the as-prepared core solution. Subsequently, a fixed amount of Zn stock solution (2.64 g Zn(OAc)$_2$, 10 mL oleylamine and 10 mL ODE) was drop by drop added into the reaction mixture in 10 batches at intervals of 15 min. Afterward, the resulting NCs solution was cooled to room temperature and precipitated by adding excess acetone and methanol. The flocculent precipitate was centrifuged at 8500 rpm for 5 min and the supernatant was decanted. This process was repeated five times and the precipitation was dried to powder for WLED fabrication. For a typical dual phosphors based WLEDs with surface mounted device (SMD) type, 0.167 g thermally curable silicone resin (OE-6551A, Dow Corning Co.) was mixed with 0.005 g CuInS$_2$ NCs dispersed in chloroform (ca. 1 mL) and 0.1 g YAG:Ce, then the solvent was removed by heating at 50 °C for 1 h. Subsequently, hardener (OE-6551B, 0.333 g) was added into the dual phosphors and silicone resin composite. The dual phosphors in silicone resin were coated onto InGaN LED chip (emission peaks: 455-457.5 nm, Sanan optoelectronics, China), and placed in thermal curing process at 150 °C for 1h. Three phosphors based WLEDs with SMD type were fabricated through similar procedure by using a mixture of three phosphors (0.025 g yellow emissive YAG:Ce, 0.06 g green emissive Eu^{2+} doped silicate (G2762) and 0.005 g red CuInS$_2$ NCs) in silicone resin. For high power (HP) devices, a mixture of 0.04 g YAG:Ce, 0.06 g G2762 and 0.01g red CuInS$_2$ NCs was used. The mass

#183500 - $15.00 USD Received 16 Jan 2013; revised 27 Feb 2013; accepted 28 Feb 2013; published 16 Apr 2013

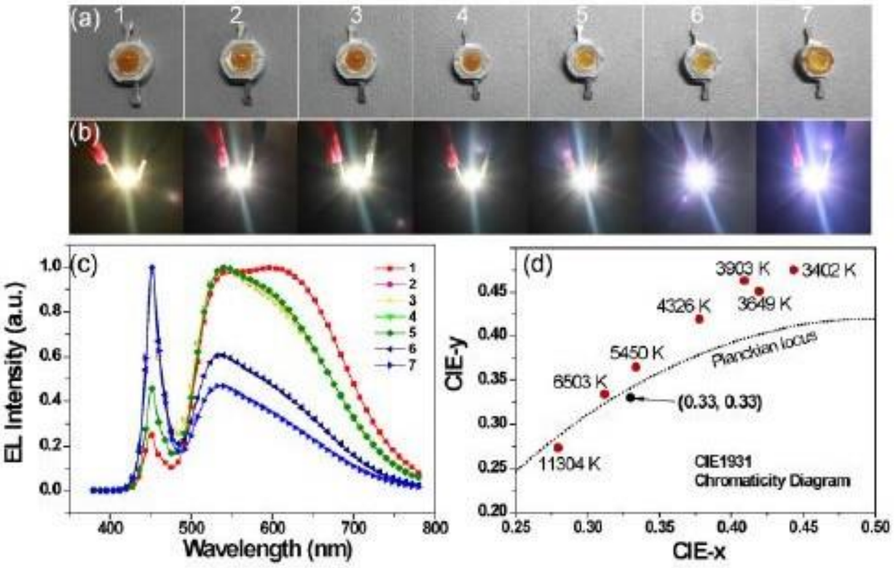


Fig. 4. Photographs of (a) the as-fabricated three phosphor WLEDs and (b) lighting operated at 350 mA. (c) EL spectra and (d) CIE color coordinates of the devices with tunable color temperatures under a forward bias current of 350 mA.

4. Conclusion

In summary, we demonstrated the potential of $CuInS_2$ based NCs as red emissive phosphor for WLEDs applications. The $CuInS_2$ based NCs with intrinsic broad emission spectra in red region not only improved the color rendering properties, but also tune the color temperature to generate warm light. The experimental results show that the CRI of YAG:Ce based WLEDs obviously improved from 71 to 82 through adding red emissive $CuInS_2$ based NCs. By further introducing green emissive phosphor G2762, the SMD devices of three phosphors based WLEDs have CRI up to ~92, luminous efficiency up to ~45 lm/W, and tunable CCT of 3800-5400 K. Furthermore, the high-power type three phosphor devices show CRI of ~80 and luminous efficiency of 50~60 lm/W with tunable CCT from 11304 to 3402 K along the Planckian locus by varying the amount of phosphors in silicone resin. The efficient generation of warm light with a CRI of 80 is acceptable for indoor lighting. These results suggest that $CuInS_2$ based NCs are competitive as the promising red emissive phosphor for warm WLEDs applications.

Acknowledgments

This work has been funded by the National Basic Research Program of China (No.2011CB933600, 2013CB328806), NSFC Research Grants (No.51003005) and Excellent Young Scholars Research Fund of . The authors wish to thank XH Wang, Z Hu and XY Zhang for experimental assistance.

#183500 - $15.00 USD Received 16 Jan 2013; revised 27 Feb 2013; accepted 28 Feb 2013; published 16 Apr 2013
(C) 2013 OSA 22 April 2013 | Vol. 21, No. 8 | DOI:10.1364/OE.21.010105 | OPTICS EXPRESS 10110

附加材料2：专家推荐表

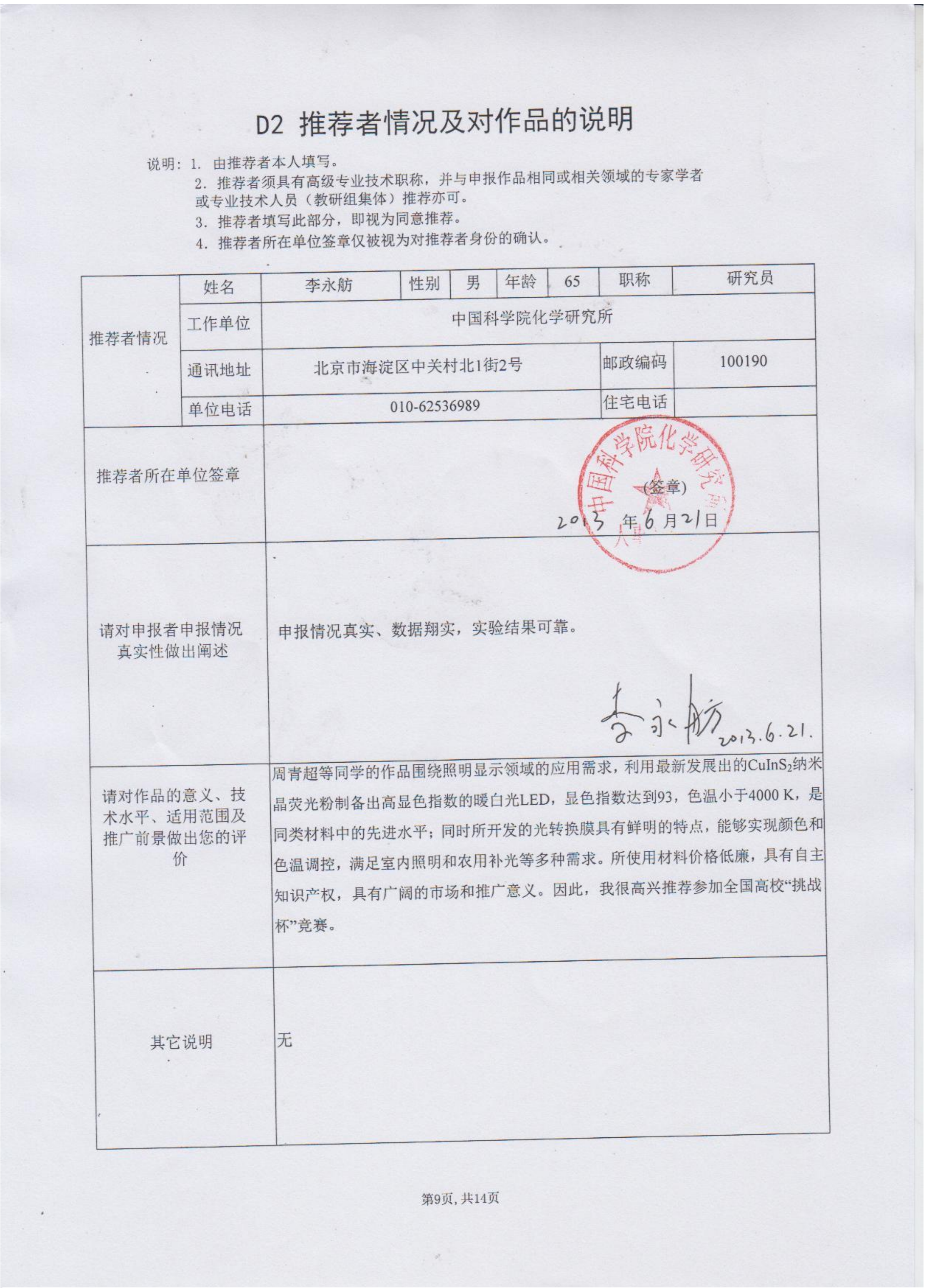
D1 推荐者情况及对作品的说明

说明：1. 由推荐者本人填写。
2. 推荐者须具有高级专业技术职称，并与申报作品相同或相关领域的专家学者或专业技术人员（教研组集体）推荐亦可。
3. 推荐者填写此部分，即视为同意推荐。
4. 推荐者所在单位签章仅被视为对推荐者身份的确认。

推荐者情况	姓名	周立伟	性别	男	年龄	81	职称	院士
	工作单位	北京理工大学光电学院						
	通讯地址	北京市海淀区中关村南大街5号					邮政编码	100081
	单位电话	010-68918966					住宅电话	010-68911748

推荐者所在单位签章	（签 章） 年 月 日
请对申报者申报情况真实性做出阐述	申报内容详实、数据可信，结论合理。 周立伟 2013年6月21日
请对作品的意义、技术水平、适用范围及推广前景做出您的评价	照明和显示是信息领域的重要产业，发展相关的新材料和新技术具有十分重要的科学意义和应用价值。周青超等同学所完成的作品，采用新型$CuInS_2$纳米晶材料制备出高性能的白光LED和多功能的光转换膜，能够适应室内照明、农用补光、液晶背光源等领域需求，具有十分重要的推广意义。因此，我很高兴推荐他们参加国家挑战杯，使他们利用该平台，展示最新的进展。
其它说明	无

第8页,共14页



D2 推荐者情况及对作品的说明

说明：1. 由推荐者本人填写。
2. 推荐者须具有高级专业技术职称，并与申报作品相同或相关领域的专家学者或专业技术人员（教研组集体）推荐亦可。
3. 推荐者填写此部分，即视为同意推荐。
4. 推荐者所在单位签章仅被视为对推荐者身份的确认。

推荐者情况	姓名	李永舫	性别	男	年龄	65	职称	研究员
	工作单位	中国科学院化学研究所						
	通讯地址	北京市海淀区中关村北1街2号					邮政编码	100190
	单位电话	010-62536989					住宅电话	

推荐者所在单位签章	（签章） 2013 年 6 月 21 日
请对申报者申报情况真实性做出阐述	申报情况真实、数据翔实，实验结果可靠。 李永舫 2013.6.21.
请对作品的意义、技术水平、适用范围及推广前景做出您的评价	周青超等同学的作品围绕照明显示领域的应用需求，利用最新发展出的$CuInS_2$纳米晶荧光粉制备出高显色指数的暖白光LED，显色指数达到93，色温小于4000 K，是同类材料中的先进水平；同时所开发的光转换膜具有鲜明的特点，能够实现颜色和色温调控，满足室内照明和农用补光等多种需求。所使用材料价格低廉，具有自主知识产权，具有广阔的市场和推广意义。因此，我很高兴推荐参加全国高校“挑战杯”竞赛。
其它说明	无

第9页，共14页