

“西光所建所六十周年暨《光子学报》创刊五十周年”专辑

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用于防伪标签的发光材料研究进展(特邀)

陈宝玖,陈昕,王礼,王轶卓,李磊,徐赛

(大连海事大学 理学院,辽宁 大连 116026)

摘 要:货币、身份证件、有价证券及商品的伪造和仿制严重威胁国家政治安全、金融稳定,侵害社会团体及个人利益。防伪技术是防范和抑制造假和克隆行为的有效手段,基于发光材料的防伪标签是当前防伪领域的研究热点。本文主要介绍近年来用于防伪标签的发光材料的研究进展,包括用于防伪标签发光材料的种类、防伪材料的发光机理、实现防伪鉴别所使用的激励源、发光防伪标签的设计方法及制作技术和防伪标签的鉴别方法等。此外,本文还对当前发光防伪材料存在的问题,以及未来发展趋势作了系统分析。

关键词:发光材料;防伪标签;下移发光;上转换;长余辉;光激励;延迟荧光;机械发光

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0 引言

在巨大经济利益驱使下,商品的仿制和伪造日趋猖獗,并对商品生产商及用户合法权益带来了严重危害。当今世界假冒商品的贸易收入为有组织犯罪收入的第二大来源,《The Business Action to Stop Counterfeiting and Piracy》报告指出世界上每年假冒和盗版造成世界经济损失高达约 1.7 万亿美元,仅次于非法药品营销收入^[1]。除经济损失外,身份证件、货币、医疗药品及卫星通讯电子产品的仿制和伪造还是威胁国家安全、经济稳定、人类健康及卫星通讯安全的重要因素,因此与非法仿制和伪造行为进行斗争已成为世界各国的长期任务。利用防伪技术对身份证件、有价证券及商业产品进行保护是一个行之有效的途径,防伪行业已成为 21 世纪的“朝阳产业”^[2]。

近年来,防伪技术研究已成为国际前沿和热点,并涌现了大量相关研究报导。根据 Web of Science 核心数据库分析发现,2017 年以前,每年发表有关防伪研究的论文数量均在 100 篇以内,2017 年发表论文突破 100 篇,以后每年发表防伪研究论文总数呈类指数增长,并在 2021 年度发表论文总数达到 470 余篇。Web of Science 核心数据库分析还发现,近年来(2014 年以来)发表的防伪有关论文涉及学科主要包括(按所占比例由大到小)材料学、应用物理学、化学、纳米科学与技术、物理化学、光学、电子工程学、凝聚态物理学、化学工程及聚合物科学等,其中有近 40% 的防伪研究与材料科学相关,可以看出防伪研究已吸引了以材料科学为主的不同领域的科学家的研究兴趣,并成为了国际科学研究热点。

防伪是指用于识别真伪并防止伪造、变造、克隆行为的技术手段。将防伪产品与潜在被制假的商品、有价证券及身份证件等相结合,可实现有效保护这些目标物的目的^[3]。防伪产品主要包括防伪标签、防伪包装、电子狗、软件密钥等,其中以防伪标签使用最为广泛,这是因为防伪标签的使用所带来的附加成本低,同时其所保护的产品范围广。防伪标签是一类具有特殊的光学、热学、磁学或化学等性质的标签,其在光、热、磁或化学试剂的作用下呈现特殊响应或变化,利用这些响应和变化可辨别与其绑定产品的真伪^[2]。在这些类别防伪标签中,以光学防伪标签最受青睐和普遍使用,光学防伪标签又可分为纯光学防伪标签(例如基于光学全息和光子晶体的标签)^[1]和具有发光特性的防伪标签(例如利用紫外 254 nm、365 nm 及红外 980 nm 光

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第一作者(通讯作者):陈宝玖(1970-),男,教授,博士,主要研究方向为稀土发光材料光谱性质。Email: chembj@sohu.com

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辐照进行鉴别的标签),其中纯光学防伪技术主要用于早期的防伪标签,而具有发光特性的防伪标签是现代新兴防伪技术的代表,并且高安全性发光防伪标签技术已成为了防伪技术领域的研究热点^[4]。

本文将对近年有关发光防伪材料研究所取得的进展进行概述,内容主要包括发光防伪标签材料的种类,发光防伪材料的发光机理,实现防伪鉴别所使用的激励源,发光防伪标签的设计方法及制作技术和防伪标签的鉴别方法等方面。此外,本文还对当前发光防伪材料存在的问题,以及未来发展趋势作了深入分析。

1 发光防伪标签材料的种类

发光防伪标签材料是发光材料家族中的新成员,它与用于照明和显示的发光材料不同。首先,作为防伪材料,它必须具有与商品化发光材料具有明显的性能区别,具有不易被利用现有发光商品材料所仿制和克隆的特征;其次,发光防伪标签材料对激发条件要求较低,一般利用商品化且成本较低的紫外灯、不同波长LED灯等进行激发;再有,发光防伪标签材料的发射光的检测要简便易行,一般是用肉眼观察发光防伪材料的发射颜色或者发光随时间的变化。需要特殊的激发源及专业检测设备的发光防伪标签材料都是不受欢迎的,因为防伪标签所保护的物体涉及的领域广泛,需要专业设备和专业人员的防伪检测会增加应用成本。从化学成分划分,当前研究较多的发光防伪标签材料分类如表1所示。

表1 发光防伪标签材料的分类
Table 1 Classification of luminescence anti-counterfeiting label materials

Classification		Representative	Reference
Rare earth and transition metal ions doped inorganic luminescence materials	Nanoparticles	NaMnF ₃ :Yb ³⁺ /Er ³⁺ @NaGdF ₄ :Eu ³⁺ ; NaGdF ₄ :Yb/Tm@NaGdF ₄ :Ce/Mn@NaYF ₄	[5-10]
		Lu ₂ O ₃ :Er ³⁺ /Tm ³⁺ /Yb ³⁺	
	Microparticles	Na ₃ ScSi ₃ O ₉ :Ce ³⁺ /Mn ²⁺	
		Sr ₂ YSbO ₆ :Eu ³⁺ ; NaLuF ₄ :Er ³⁺ /Yb ³⁺ @glass	
Semiconductor quantum dots	Amorphous powders		[11-14]
	Perovskite	CsPbBr ₃ @Cs ₄ PbBr ₆ /SiO ₂	
	ZnO	ZnO	
Luminescence carbon materials	Cd-based semiconductor	CdTe, CdSe, CdS	[15-18]
	Carbon dots		
	Carbon nanodots		
	Carbon quantum dots		
	Carbonated polymer		
Metal-organic frameworks	Graphene		[19, 20]
		Eu/Tb(BTC), Tb/Eu(tcptpy)	
Organic luminescence materials		Cellulose, Cucurbituril, Polymer fiber, TMS(trimethylsilyl) modified diarylethene, Small-molecule-doped organic crystals	[21-26]
Complex and hybrid materials		NaYF ₄ :Er, Yb(Tm)/carbon dots	[27-30]

表1中第一类发光防伪标签材料是离子中心掺杂的无机荧光粉材料,其掺杂的离子发光中心主要为稀土离子和过渡金属离子。从材料的晶体学结构划分可分为多晶粉末和非晶粉末材料,多晶荧光粉又分为纳米晶和微米晶,其中也包括核壳结构纳米晶,非晶粉末是将稀土或过渡金属掺杂的玻璃或陶瓷经粉碎后得到的粉末。

第二类发光防伪标签材料是半导体量子点,其中以CsPbX₃(X=Cl, Br, I)量子点为主流,也包括他们的核壳粒子及组分中部分元素被等价取代的钙钛矿量子点。另外,ZnO、CdTe、CdS及CdSe等量子点材料也有用于防伪标签的研究报导。

第三类发光防伪标签材料是发光碳材料,发光碳材料是继碳纤维和石墨烯之后被发现和广泛关注研究的新型发光材料,其由碳元素组成,一般粒子尺寸小于10 nm,是一种零维材料,粒子表面富集大量的羟基、

羧基和环氧基。当前对发光碳材料的命名和分类尚存在争议,文献中常用的命名有碳点(carbon dots)、碳量子点(carbon quantum dots)及碳纳米点(carbon nanodots)等,本文认为这些零维发光碳材料在本质上都是同一类材料,目前学术界尚无严格的区分。

第四类是金属有机框架材料,具有发光特性的金属有机框架材料是近年来发展起来的一类新兴发光材料,其由金属离子或金属离子团簇埋在有机分子骨架结构中形成的稳定结构,其中金属离子可以是稀土和过渡金属离子中心,这类材料一般具有较高的孔隙率,大的比表面积和结构可设计剪裁性。

第五类用于发光防伪标签的材料是有机发光材料,该类材料包括有机发光聚合物、发光纤维素、有机超结构材料、具有光致变色和超长磷光的有机小分子及金属有机配合物等,这些材料具有独特的发光特性,是进行发光防伪标签开发的新兴材料。与无机发光材料相比,有机发光材料结构更复杂,种类也更丰富,发光性能可调控的空间更大,可为发光防伪标签提供更丰富的材料选择。还应该明确的是光致变色材料在防伪领域应用并非基于其发光性质,这类材料是在光照下产生结构改变,致使其吸收特性发生改变,进而产生表面颜色变化。

第六类为前面五类发光材料中两类以上的复合材料或杂化材料。复合材料是指将具有不同性质的材料进行组分优化组合使形成的材料具有某种或几种更优异性能的材料,复合材料各组分间可以是物理混合。杂化材料一般是由有机和无机功能结构单元或有机与无机组分通过化学结合在一起形成的材料,杂化材料能够发挥有机和无机组分的双重优化性能。

在以上六类材料中,离子中心掺杂的无机材料物理和化学性质更稳定,发射波长范围覆盖广,可选择的激发波长丰富,包括从紫外-可见到近红外波长。另外,三价稀土离子掺杂材料的发射谱带窄;发光碳材料的发光稳定性相对较差,发射波长基本在可见范围,有效激发波长基本在紫外和近紫外;半导体量子点材料作为发光防伪材料的研究相对较少,激发波长多在紫外和可见,发射波长多在可见和近红外;金属有机框架材料、有机发光材料和杂化材料发射谱带一般较宽,该类材料光谱性能可调控灵活性高。

2 发光防伪标签材料的发光机理

不同的发光材料在受到外界激励源的刺激后,其内部激发态运动的规律也可能不同,也就是受到激发后材料内部能级的布居变化过程不同,根据激发过程及激发态布居变化过程的不同,以上六类发光防伪材料的发光机理可分为下移发光、上转换发光、长余辉发光、光激励发光、延迟荧光及机械发光等。

2.1 下移发光

发射波长长于激发波长的过程,是斯托克斯过程,与量子剪裁过程不同,是一个激发光子最多产生一个发射光子的过程。图1(a)给出了下移发光过程的示意图,发光材料吸收 E_x 激发光子,跃迁到高激发态,然后无辐射弛豫到较低激发态,低激发态发射 E_m ①或②光子,以上介绍的六类材料均可能发生下移发光^[5, 7, 8, 11, 17, 21, 31, 32]。

2.2 上转换发光

发射波长短于激发波长,是反斯托克斯过程,产生一个发射光子需要两个或更多个激发光子的过程,多见于稀土离子掺杂的材料中。稀土掺杂材料的上转换发光可通过级联能量传递、激发态吸收、合作敏化、双光子吸收激发及光子雪崩等过程实现,其中理论上以通过能量传递实现上转换发光效率最高,激发态吸收过程次之,其他的上转换过程的效率均与能量传递上转换过程存在数量级的差别^[33, 34]。图1(b)和(c)是能量传递上转换和激发态吸收上转换过程的示意图。在能量传递上转换过程中,离子a吸收激发光子,然后通过两次能量传递过程使离子b达到高激发态并产生短波长发射。在激发态吸收上转换过程中,发光中心先吸收一个光子达到中间亚稳态,然后处于亚稳态的发光中心再吸收一个激发光子达到高激发态并产生上转换发射。

2.3 长余辉发光

吸收激发光能量并储存,在激发停止后发光仍能持续,长余辉发光一般认为与材料中缺陷相关,对于一些长余辉材料,其长余辉产生机制仍存在争议。目前报导的长余辉发光主要有空穴传输、电子空穴共传输及“隧穿”效应等三种模型^[35, 36],图1(d)和(e)给出了电子空穴共传输和“隧穿”效应模型示意图。在电子和

空穴共传输型长余辉材料中,材料吸收光子后将电子由价带激发到导带,在价带留下一个空穴,然后价带空穴和导带电子分别传输到电子和空穴陷阱并被束缚,被束缚的电子和空穴通过吸收晶格热从陷阱中溢出并通过导带和价带传递给发光中心,产生余辉发射。在“隧穿”效应余辉材料中发光中心吸收激发光子将电子激发到导带,然后束缚在电子陷阱中,陷阱中电子通过隧穿再回到发光中心激发态,激发态辐射光子产生余辉。长余辉材料多为稀土及过渡金属离子中心掺杂的无机荧光粉材料。

2.4 光激励发光

光激励发光过程的储存能量机理与长余辉发光过程类似,材料吸收高能激发光子后将电子激发到导带,然后束缚在陷阱中,这个陷阱比长余辉材料的陷阱更深,因此被束缚的电子不能够通过吸收晶格热而逃脱陷阱的束缚。当用红外光辐照样时,被束缚的电子吸收红外光子的能量从陷阱中逃脱并被发光中心俘获,发光中心退激发后产生荧光^[37-40]。光激励发光材料多为稀土中心和过渡金属离子中心掺杂的发光材料。光激励发光材料多为离子中心掺杂的无机发光材料。

2.5 机械发光

机械发光是材料在机械力的作用下产生发光的现象,机械力包括压力、摩擦力等。机械发光被发现已有上百年的历史,但到目前对机械发光机理的认识仍不够清晰。机械发光在有机材料和无机材料中都被观察到,多数机械发光材料存在与长余辉和光激励发光材料类似的陷阱^[41-46]。

2.6 延迟荧光

图1(f)为荧光、磷光和延迟荧光发射机理。材料吸收激发光子后由基态跃迁到单重态,如果电子由单重态回到基态就产生荧光发射,如图1(f)中①过程;如果电子通过系间窜越(Inter System Crossover, ISC)到三重态,由于三重态到基态的跃迁是自旋禁戒的,因此三重态到基态的跃迁产生磷光,如图1(f)中③过程所示;如果电子由三重态通过反向系间窜越(RISC)回到单重态后在产生跃迁就是延迟荧光发射,如图1(f)中②过程所示。延迟荧光多发生在有机发光材料和发光碳材料中^[47-50]。

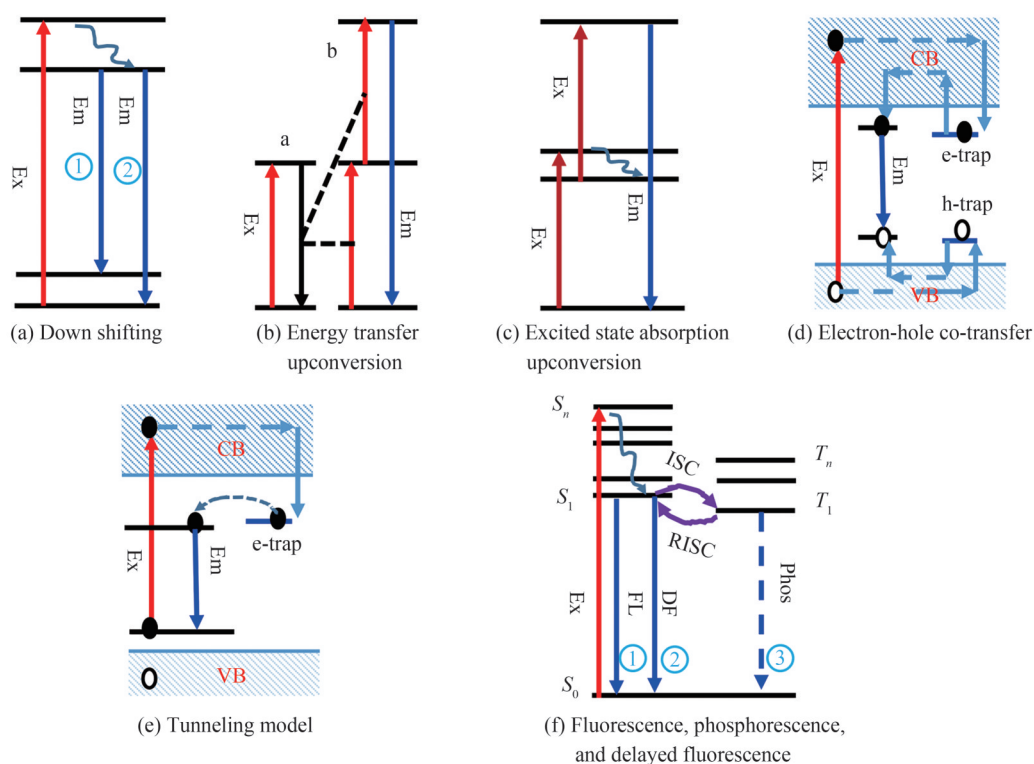


图1 发光防伪材料的发光机理

Fig. 1 Luminescence mechanisms for luminescence anti-counterfeiting materials

3 发光防伪标签识别用激励源及化学试剂辅助

发光防伪标签的识别是在外界激励的作用下使标签的颜色或图案产生变化,或者在外界激励的作用下颜色或图案随时间产生变化。因此,鉴别防伪标签需要外界激励源,对于一种防伪标签,为了增强其防伪的可靠性有时需要两种或以上激励源单独或同时进行作用,每种激励源使防伪标签产生不同的变化,或产生易于常规发光材料的变化。当前研究报导所用的激励源主要有以下几种。

3.1 光激发源

文献报导的发光防伪标签识别所用激励源以光波为主,所用不同波长和类型的光源包括:日光,即太阳光;紫外灯,波段为 254 nm 和 365 nm;LED 灯,波长多为 365 nm、395 nm 及 465 nm;红外激光光源,波长多为 980 nm,个别为 808 nm 及 1 550 nm 等^[30, 51-57]。其中日光、紫外灯和 LED 灯主要用于长余辉、光激励发光、延迟荧光等材料的储能激发;下移发光防伪材料的激发主要使用紫外灯和 LED 灯;红外激光主要用于上转换防伪材料和光激励防伪材料的防伪信息鉴别。

3.2 机械力

机械力激励主要用于机械发光防伪材料制作的防伪标签的识别,一般是对防伪标签施加外部压力或摩擦力,在外部压力的作用下防伪标签会产生光发射^[41, 43, 45, 58]。

3.3 热激励

对防伪标签进行加热使其颜色产生变化,这种颜色改变是由于防伪标签材料结构依赖的光吸收特性的改变,或者是由于防伪标签材料热释光发射导致^[59-62]。

3.4 化学试剂辅助

在防伪标签验证时,通过向发光防伪标签上添加化学试剂(如 $\text{CH}_3\text{NH}_3\text{Br}_3$ 、 H_2O 及酸或碱性试剂等),在化学试剂辅助作用下使其可观测性质产生变化来鉴别真伪,一般用于有机发光材料防伪标签鉴别^[22, 63-65]。

4 发光防伪标签制作与设计方法

4.1 防伪标签图样制作方法

光学防伪标签可应用于金属、非金属及纸张类衬底上,是最受欢迎,也是应用最为广泛的防伪方法。防伪标签本身的制作技术已非常成熟,因此有关防伪标签制作技术的研究报导较少。本文仅就国内外发表的研究论文中所采用的防伪标签的制作方法进行介绍,而不涉及防伪标签工业化生产中所采用的制作技术。近年来,学术论文中所使用的防伪标签制作技术主要有以下论述的几种。

4.1.1 图章与手工绘制法

该方法是用含有防伪材料的浆料在纸张上手工绘制图样,或将浆料涂覆在预制图样的图章上,然后在纸张上印制图章图案。这种方法简单易行,成本低廉,该方法为开展发光防伪材料的前期研究带来了较大方便,但该方法制作高精度防伪图样比较困难^[66]。

4.1.2 丝网印刷术

丝网印刷是一种工序非常简单,成本低廉,生产效率很高,制作图案的精度较高,适合工业化生产的技术,该项防伪标签制作技术的缺点是不适合颜色复杂的图案印制^[28, 67-69]。

4.1.3 喷墨打印技术

该技术是一种成熟的防伪标签制作技术,可实现高分辨率防伪图像的制作,并可制作全彩色防伪图像。当前研究人员将含有防伪材料的墨水直接取代商品喷墨打印机的墨水加注到喷墨打印机的墨盒中,实现防伪标签打印^[13, 16, 50, 54, 58, 70-72]。

4.1.4 气溶胶喷射打印技术

气溶胶喷射打印是一种新型的打印技术,不仅可实现高精度二维(2D)平面图样的打印,还可实现三维(3D)空间图形打印。该项防伪标签制作技术的成本较高,对防伪材料浆料要求也较高^[73, 74]。

4.2 发光防伪标签图样设计

当前报导的发光防伪标签的设计可以总结为三个方面的组合^[53, 75-78](如图 2 所示):一是激励源,激励源就是上面介绍的三类,对于一个防伪标签,可以使用三类激励源中的一种或多种,此外,一些特殊材料

制作的防伪标签需在化学试剂辅助的条件下进行外界激励才可产生有效响应。其中光激发源包含多个波长,如紫外 254 nm、365 nm、395 nm、可见的 465 nm 及红外 808 nm、980 nm 及 1 550 nm。对于一种防伪标签,它的有效激发波长可以是这些激发波长中的一种或多种,所用的激发波长越多防伪标签的安全性也越高,但同时成本也越高,另外实际应用难度也越大。第二方面是在激励源作用下防伪标签的响应,发光防伪标签的响应主要有两个,一是发光颜色,当采用不同的激励源作用防伪标签时,防伪标签会显示不同的颜色,也可以是两种激励源同时作用时显示某种颜色;二是发光强度和颜色随时间变化,当某种激励源作用防伪标签后,标签发光亮度和颜色会随着时间改变,这一改变的时间范围从 1 s 到数小时不等。第三个方面就是防伪标签图案的设计,也就是将不同激励和不同响应的一种或多种发光防伪材料采用 4.1 中介绍的方法制作特征的防伪图案,当前文献报道较多防伪图案有七段码(Seven Segment Code, SS Code)、条码(Bar Code)、二维码(Quick Response Code, QR code)、组织徽标(logo)及具有特殊意义的图像(Image)等。

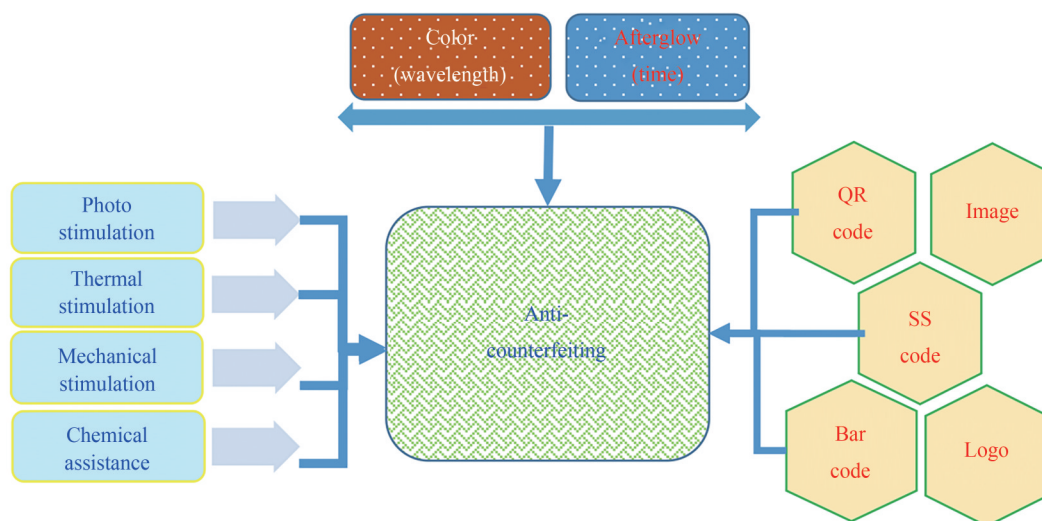


图2 防伪标签设计要素

Fig. 2 Key factors for designing anti-counterfeiting labels

可以看出,一个防伪标签是由一种或多种发光防伪材料采用喷墨打印等技术制备的二维图案,该图案对一种或多种激励方式产生独有的响应,通过对激励方式、响应情况和预设图案编码等对防伪标签进行识别真伪。

4.3 图样隐藏的防伪标签

一些用于防伪标签的发光材料具有自然体色,利用这些材料制作的防伪标签在自然光照下会呈现出图案。为了达到视觉美观目的,或者在特殊的情况下需要将防伪标签图案隐藏起来,这就需要与发光材料体色相同的颜料(并在该标签识别用的激励源作用下不产生响应)将非防伪材料覆盖的区域进行填充,致使整个标签区域在自然光照下颜色一致^[5, 30]。

4.4 发光防伪标签案例

本文已对发光防伪标签材料及其相关研究进展做了概括性阐述,为了使读者对发光防伪材料在防伪标签应用方面有更直接的认识,这里列举几种发光防伪材料制作防伪标签的实例,但还应该指出的是发光防伪标签材料及其应用涉及较多的具体应用技巧,限于文章的篇幅不能一一阐述,有兴趣读者可阅读本文参考文献。

4.4.1 稀土及过渡金属离子中心掺杂无机材料防伪标签应用

研究者开发了一种 Mn^{4+} 及 Er^{3+} 共激活 $\text{Ba}_2\text{GdTaO}_6$ 荧光粉^[79],该荧光粉采用了过渡金属离子和三价稀土离子作为激活中心,将二者掺杂在 $\text{Ba}_2\text{GdTaO}_6$ 基质中可同时实现在不同波长激发下的下移发光和上转换发光。作者利用该荧光粉采用丝网印刷技术绘制了三叶草防伪标签图案,如图 3。在自然光下,防伪标签呈现与衬底不同的白色,如图 3(a);在 365 nm 灯照射下防伪图案为暗红色,如图 3(b);在 1 550 nm 光辐照下防伪

图案为黄绿色,如图3(c);在980 nm光辐照下,防伪图案为浅绿色,如图3(d)。

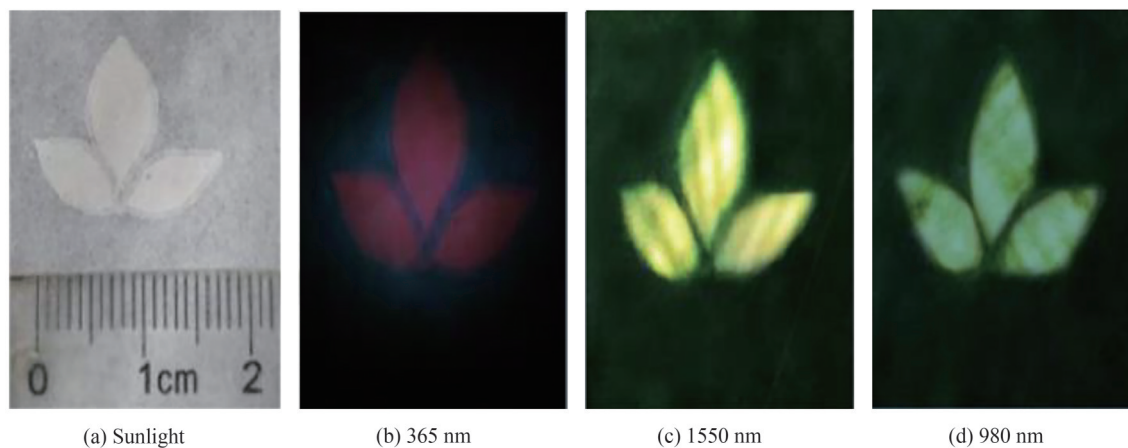


图3 不同光辐照下防伪标签照片

Fig. 3 Photos of anti-counterfeiting label under different irradiations

4.4.2 半导体量子点防伪标签应用

HAN Wenjuan等采用微波加热技术合成的 $Ti_3C_2T_x$ MXene量子点^[80],该量子点在不同波长激发下发射光谱中心位置产生较大移动,也就是发射颜色随着激发波长产生变化。作者利用所合成的量子点在商品打印纸上绘制的熊猫图案作为防伪标签,在日光照射下图案在打印纸上几乎不可见,如图4(a)所示,因此该防伪材料所制作的防伪标签在白色背底下可实现自然隐藏。在365 nm辐照图案时,打印纸上出现了浅蓝色熊猫图案,如图4(b)所示;用254 nm辐照时,打印纸上出现了紫色熊猫图案,如图4(c)所示。

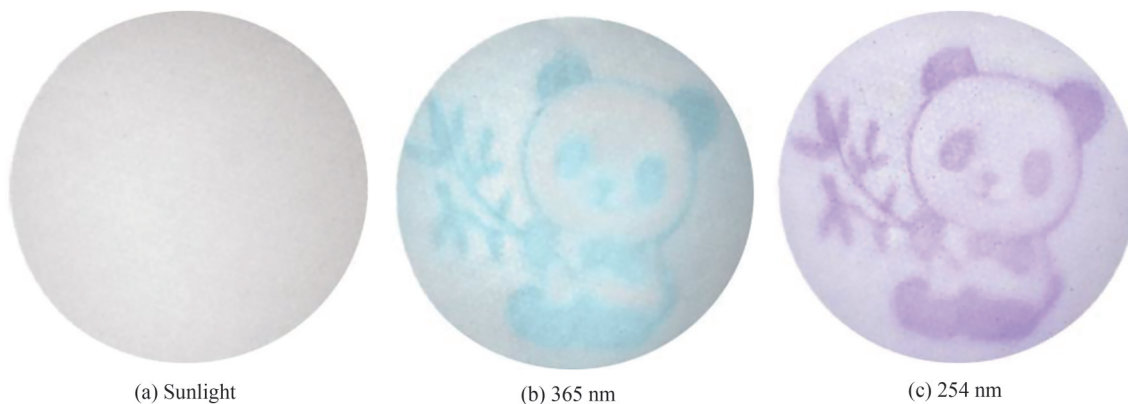


图4 不同光照下利用 $Ti_3C_2T_x$ MXene量子点制作防伪标签照片

Fig. 4 Photos of anti-counterfeiting label under different irradiations by $Ti_3C_2T_x$ MXene

4.4.3 碳点发光材料的防伪标签应用

JIA J等以对氨基苯磺酸为原料,采用水热反应方法制备了尺寸为5 nm左右的碳点材料^[81]。研究发现合成的三种碳点材料中C=O和C-N键所占比例不同,从而导致能带结构不同,进而发射光谱的中心位置也不同。作者将三种不同发射的碳点材料涂覆在三种剪纸上,如图5(a)中1-3为在日光下三种不同碳点涂覆的三种剪纸,可以看出剪纸颜色略微偏离白色。图5(b)为三种碳点涂覆的三种剪纸在365 nm光辐照下的照片,可见不同量子点涂覆的剪纸颜色不同,因此,这三种碳点可以用于三基色油墨,通过打印制作防伪标签,该标签在日光下呈现接近白色的图像,在紫外365 nm灯辐照下可观察到彩色图案,达到防伪目的。

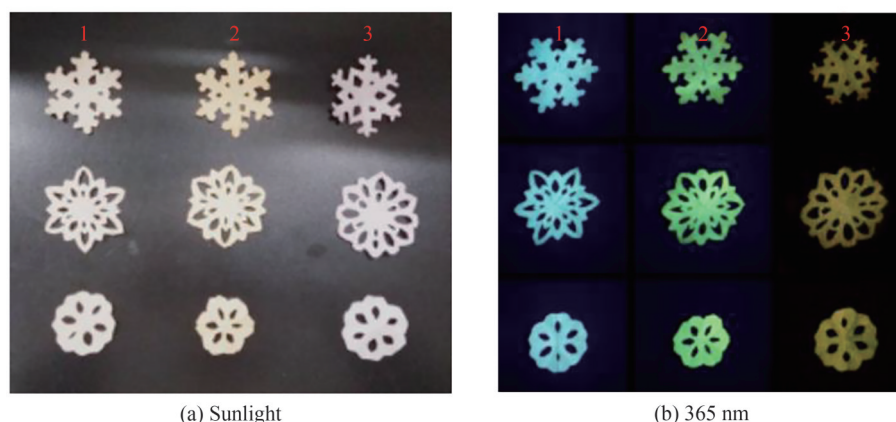


图5 三种不同碳点涂覆的剪纸照片

Fig. 5 Photos of the paper-cuts coated by three different carbon dots

4.4.4 金属有机框架材料防伪标签应用

WANG Haiping 等合成了 Eu-MOF (Eu-金属有机框架) 材料^[82], 并将 Eu-MOF 和 MAPbBr₃ (钙钛矿 CH₃NH₃PbBr₃) 引入到纸浆纤维 (PFs) 中并均匀涂覆在打印纸上, 在 254 nm 激发下纸张呈红色, 这是由于 Eu³⁺ 的本征发射导致。将 MAPbBr₃ 作为油墨在涂覆有 Pb/Eu-MOF@PFs 的纸张上绘制防伪图案, 然后在 254 nm 辐照下基本观察不到防伪图案, 但在 365 nm 光照下可观察防伪图案。当将防伪标签用水浸湿后, 由于 MAPbBr₃ 在极性分子液体中的不稳定性, 导致防伪信息消失, 但是书写信息已被存储在纸张上。当用 MABr (CH₃NH₃Br) 油墨在纸张上涂覆后, MAPbBr₃ 再次生成, 在 365 nm 辐照时防伪图案再次出现, 并且在用 254 nm 辐照时仍然是红色无图案图像。以上描述过程如图 6 所示。

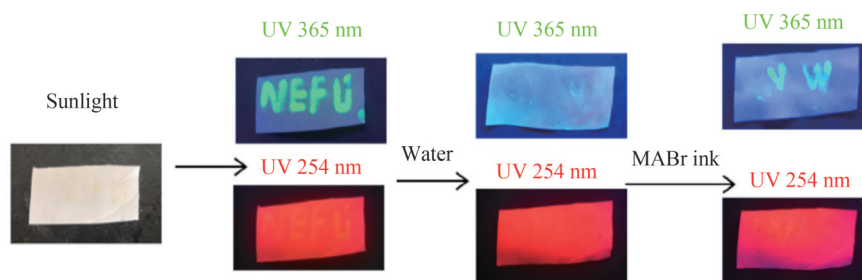


图6 金属有机框架材料制作防伪标签的擦除和写入过程

Fig. 6 Erasing and writing processes for the anti-counterfeiting label produced by metal-organic framework material

5 总结与展望

综合以上对发光防伪标签材料、发光机理、防伪标签检验所用激励源及防伪标签设计方案等方面的分析, 可以看出发光防伪标签具有丰富的可选择材料体系, 具有灵活多样的激励源和高度自由的防伪图案设计。1) 防伪标签材料方面。离子中心掺杂无机发光材料的研究历史悠久, 科学家们开发了大量的上转换荧光粉、不同发射颜色的下移发光荧光粉、长余辉材料等, 因此开发与已有商品荧光粉性能迥异的新型发光防伪标签材料仍是巨大挑战。发光碳材料的稳定性一般较差, 因此通过杂化及复合等手段提升其稳定性是可能将其推向实用的途径。有机发光材料, 如超分子框架材料、聚合物材料等的发光性能可调控性强, 是未来发光防伪标签材料重要发展方向。2) 激励源配置方面。当前研究报导的绝大多数发光防伪标签均利用了光致发光材料, 因此在对防伪标签进行识别时均需要相关光源, 例如波长为 254 nm、365 nm、395 nm、808 nm、980 nm 或 1 550 nm 等光源。虽然这些波长光源都有市售商品, 但在防伪标签所保护对象的发售、营销、流通和使用过程中均需配备这些光源才能进行鉴别, 有些时候甚至需要两种或以上波长的光源, 这样显

然是不方便的。因而利用机械发光防伪材料和利用常用试剂(如水、小苏打溶液、食用白醋等)辅助进行检验的防伪材料将更受用户欢迎^[22, 63, 65]。但是,应该指出的是利用试剂辅助进行检验的防伪材料的稳定性应给与重点考虑,还有所用化学试剂是否方便获取也应予以重视。3)仿制与克隆方面。当前文献报导的无论是下移发光、上转换发光、光激励发光还是长余辉发光材料制作的防伪标签,它们的发射光谱均在可见区,这主要是为了防伪标签鉴别的方便,也就是用肉眼直接观察防伪图案而无需专用设备,但这也带来了较大的被仿制隐患,这是因为当前不同波长激发下的可见区的上转换发射材料、下移发射材料、长余辉材料等均已商品出售,因此避免利用现有商品荧光粉对防伪标签的仿制和克隆仍是一个挑战。4)防伪标签鉴别方面。当前文献报导的绝大多数防伪标签的识别都是以现场的颜色、余辉和图案的观察方式实现,随着5G通讯技术的普及可以将现场鉴别与互联网验证相结合,例如防伪标签可以采用随机图形编码,做到每个商品一个图形编码,然后通过互联网进行验证;也可以将随机数字编码和防伪标签结合使用,在现场完成光学防伪鉴别,在线上完成数字编码授权。

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Progress in Luminescent Materials for Anti-counterfeiting Labels (Invited)

CHEN Baojiu, CHEN Xin, WANG Li, WANG Yizhuo, LI Lei, XU Sai
(School of Science, Dalian Maritime University, Dalian, Liaoning 116026, China)

Abstract: The present international situation becomes complicated, and meanwhile terrorism and illegal organization activities are rampant, moreover counterfeiting and imitation of currencies, identity documents, securities, and commodities seriously threaten national political security and financial stability, and infringe on the interests of social organizations and individuals. Anti-counterfeiting technique is an effective means to prevent and suppress counterfeiting and cloning, therefore anti-counterfeiting labels based on luminescent materials turn into a research hotspot in the field of anti-counterfeiting. This review mainly introduces the research progress of luminescent materials for anti-counterfeiting labels in recent years, including the types of luminescent materials for anti-counterfeiting labels, the luminescent mechanism of anti-counterfeiting materials, the excitation sources used to realize anti-counterfeiting identification, the design method and manufacturing techniques of luminescent anti-counterfeiting labels, and the identification methods of anti-counterfeiting labels. In addition, this paper also systematically

analyzes the problems existing in the current luminous anti-counterfeiting materials and the future development trend.

In recent years, almost all kinds of luminescence materials have been examined to be used in anti-counterfeiting labels. The more popular luminescence materials to be used include rare earth ions or transition metal ions doped inorganic phosphors, semiconductor quantum dots materials, luminescence carbon materials, metal-organic framework materials, pure organic luminescence materials, and complex and hybrid materials. The rare earth ions or transition metal ions doped phosphors exist as nano-, micro-crystals, or amorphous powders. The crystals can be pure phased or core-shell structured. The amorphous powders are usually derived from the ceramic or glassy bulks via crushing or grinding processes. The semiconductor quantum dots materials that have been examined for luminescence anti-counterfeiting labels mainly include Cd-based quantum dots, lead cesium halides perovskites, and zinc oxides. In the literatures, the luminescence carbon-based materials are often defined as carbon dots, carbon nanodots, and carbon quantum dots. Up to now, there is no clear clarification for the differences between these carbon-based luminescence materials. In our opinion, these are the same. Moreover, some other luminescence carbon-based luminescence materials, like carbonated polymers and graphene have also been used in luminescence anti-counterfeiting labels. The luminescence metal-organic frameworks have also been investigated for applications of luminescence anti-counterfeiting labels. The metal specimen can be rare earth ions and transition metal ions which act as luminescence ions also. Very plentiful pure organic luminescence including cellulose, cucurbituril, polymer fiber, and small-molecule-doped organic crystals have also widely been tested for luminescence anti-counterfeiting label applications. It should be pointed out that the complex and hybrid materials composed of the above-mentioned materials are also preferable in luminescence anti-counterfeiting labels.

The luminescence mechanisms for the above-stated luminescence anti-counterfeiting materials mainly contained down-shifting emission, up-conversion, long afterglow, photo-stimulated luminescence, mechano-luminescence, and delayed fluorescence. The down-shifting emissions can be achieved in the all mentioned luminescence anti-counterfeiting materials. In most cases, the excitation wavelengths are located in the ultraviolet region, and emissions full usually in the visible region. The up-conversion luminescence requires usually near-infrared wavelengths, for example, 808, 980, and 1 150 nm, as the excitation sources, and the emissions are visible as well. The up-conversion emissions are usually realized in rare earth ions doped inorganic materials. The afterglow phosphors, photo-stimulated materials, and mechano-luminescence materials exhibit similar properties except for the excitation sources. In these materials, the defects are usually involved, and the electron and hole traps also exist and play important roles. The delayed fluorescence is usually observed in carbon-based luminescence materials and organic luminescence materials.

The luminescence anti-counterfeiting labels are identified under stimuli sources. In this review, the stimuli sources used for identifications were also introduced. The stimuli sources include photo stimuli source, mechano-stimuli source, thermos-stimuli source. Amongst all these stimuli sources, the photo stimuli source is the most widely used one. The wavelengths of the photo stimuli sources contain sunlight, 254, 365, 395, 465, 808, 980, 1 060, and 1 550 nm. These excitation photons usually come from ultraviolet lamps, light emitting diodes, and diode lasers. Sometimes, identification of the luminescence anti-counterfeiting labels is carried out in assistance of some chemicals, for instance, $\text{CH}_3\text{NH}_3\text{Br}_3$, H_2O , vinegar solution, and baking soda solution.

In this review, the commonly used painting techniques for producing luminescence anti-counterfeiting labels were also presented. The widely adopted producing methods of the anti-counterfeiting labels mainly include drawing/stamping method, screen printing technique, laser jet printing technique, aerosol jet printing technique, and so on. Amongst these techniques, the drawing/stamping method is low-cost and easy-operated and is most widely used in research work. The screen printing technique is simple and mature, but the resolution of the anti-counterfeiting images produced via this technique is usually low. The laser jet printing technique is just transplanted from the laser jet printers. With the use of this technique, the inks of the laser jet printer are replaced by the inks containing the luminescence anti-counterfeiting materials. The aerosol jet printing technique is newly developed, with which three-dimensional images can be produced.

At the end of this review, the present status of the luminescence anti-counterfeiting materials was

concluded. The problems and obstacles to developing luminescence anti-counterfeiting labels were summarized. Some ideas for future progress were also proposed. It was figured out that the emission wavelengths for the present luminescence anti-counterfeiting materials are mainly in the visible region, thus resulting in easy counterfeiting and cloning. Therefore, developing novel luminescence anti-counterfeiting materials with emitting wavelengths other than visible wavelengths may be a good proposal. In many articles, more than one stimuli source were used, thus in fact is not a good way since the multi-excitation sources would result in complicated identification and high cost. Therefore, developing chemical-assisted luminescence anti-counterfeiting materials is more significant and meaningful. It should also be pointed out that the luminescence anti-counterfeiting materials with similar spectral properties to the commercialized phosphors are useless and dangerous since the counterfeiting and cloning behaviors are easy by using the commercialized phosphors in this sense. Finally, the combination of online and offline identifications is suggested while the 5G technique is widely used.

Key words: Luminescence material; Anti-counterfeiting label; Down-shifting luminescence; Upconversion; Long afterglow; Photo-stimulation; Delayed fluorescence; Mechano-luminescence

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