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新一代有机电致发光材料与器件

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摘要 针对我国有机发光二极管(OLED)显示领域对低成本、高性能材料及简约器件制备工艺的重大迫切需求, 提出不含贵重金属的纯有机材料体系及相关器件研究计划; 开发并完善自主知识产权的新一代发光材料/主体材料体系, 使发光效率和寿命达到实用化的水平; 掌握新一代发光材料的发光机制、构效关系、激发态过程及其调控规律, 实现兼顾结构简单、高效率、长寿命的新型器件结构, 明确其内在物理机制和规律, 为高性能材料和器件开发提供科学指导和解决方案, 并在此基础上实现显示器件的优化设计、集成和可控制备.

关键词 有机发光二极管, 有机发光材料, 激发态, 稳定性, 显示器件

有机发光二极管(OLED), 因具有全固态、像素点自发光、广视角、超快响应、丰富的色彩表现力、有潜力实现超低成本喷墨打印工艺和可制备柔性超薄器件等优势, 被誉为“梦幻显示”技术, 成为当前占市场主导地位的液晶显示技术的有力竞争者, 受到了学术界和产业界的高度重视. 自20世纪80年代以来, 在大量研究机构和企业的共同努力下, 小尺寸OLED显示屏已经广泛应用于智能手机、智能手表、智能手环、以及车载仪表盘等诸多方面. 大尺寸OLED电视的产业化进程也正在加速, 韩国LG公司已经陆续推出55和70英寸OLED电视产品, 厚度不足5 mm, 色彩饱和度和对比度高, 响应速度快, 成为高端LCD电视强有力的竞争者. 我国整机企业长虹、创维等也纷纷推出国产品牌的OLED电视, 但OLED模组需要进口. 我国显示面板企业京东方、华星光电、维信诺也展示了自主研发的12, 30以及55英寸等OLED面板样机, 表明我国正在加速推进OLED显示屏进入量产阶段. 除在显示上的应用外, 白光OLED作为一种发光柔和的面状光源, 具有少的蓝光成分、高的显色指数、以及光色接近自然太阳光的特点, 是一种理想的健康护眼光源, 与具有高亮度、点光源特点的无机发光二极管(LED)形成了很好的互补, 特别适合于室内的大面积照明, 在未来照明领域中具有光明的应用前景, 也正在逐步发展成熟. 当前OLED显示与照明产业正处于蓬勃发展的朝阳阶段.

1 国内外现状及趋势

OLED材料及器件的研究思路通常以发光材料为中心, 并开发与之相匹配的主体材料、载流子传输材料等辅助材料, 使发光材料性能最大化, 从而获取高性能的OLED器件. 因此, 发光材料的开发往往在OLED技术中处于上游最为核心的地位. 受自旋量子统计规则的限制, 业内最早开始发展的基于传统荧光材料的OLED的最大内量子效率仅为25%左右[1]. 该效率瓶颈在1998年由于磷光材料在OLED上应用的突破性进展而被打破[2,3]. 对于重金属配合物构成的磷光材料, 由于重原子引起的自旋轨道耦合效应, 使得电场下产生的激子可100%以磷光辐射发光的形

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式被利用. 因此, 磷光OLED器件的内量子效率可以达到100%. 由于长寿命深蓝光磷光OLED的研发相对滞后, 目前商用OLED显示普遍采用的是“蓝光荧光材料+红光和绿光磷光材料”的技术方案. 然而, 磷光材料中含有较为昂贵的稀有或贵金属, 增加了OLED 显示面板的材料成本.

1999年, Cao等人[4]首次报道了共轭高分子体系中单线态激子形成比例可以达到50%. 其后, 多个研究组报道了激子利用率远超25%的荧光器件, 证明了突破经典激子统计在实验上和原理上的可能性. 但是, 共轭高分子体系的稳定性、结构性质关系不明确等问题, 使其实际器件应用受到制约, 2001年后激子统计的研究相对地沉寂了下来. 2009年, 日本九州大学将热活化延迟荧光材料成功应用于OLED器件, 重新唤起了关于突破激子统计的研究[5,6]. 这类材料的激子利用效率可达100%, 且不含稀有或贵金属元素, 源合成材料来源广泛, 有望实现低成本规模化生产. 从发光材料的发展时间上划分, 传统荧光材料、磷光材料依次被称为第一、第二代OLED发光材料. 而不含稀有或贵金属元素、且内量子效率同样有望达到100%的新型纯有机发光材料则被称作新一代有机电致发光材料.

鉴于有机发光显示是新型显示领域备受关注的高新技术, 蕴含着巨大的商业前景和发展机遇, 国外一直封锁关键材料、关键技术和关键设备. 以材料为例, 高质量OLED材料的专利大都被国外公司掌握. 日本出光兴产公司的主客体蓝光材料体系具有商业化实用价值, 但无论学术交流还是商业宣传, 关键材料全部采用代号, 只报道器件效率和工作寿命, 而不报道任何分子结构与物性特征. 德国Merck公司和日本住友化学公司在高分子发光材料方面处于国际领先地位, 只有进行技术转让才能提供配套材料供应. 磷光材料的技术专利则主要掌握在美国UDC手中. 上述部分事例充分说明, 有机发光显示材料是制约有机电致发光显示屏成功商业化的关键因素之一, 也成为制约我国OLED产业发展的瓶颈, 而掌握关键材料的核心技术与知识产权的唯一途径是依靠自主创新. 因此, 我国关于有机平板显示的定位应该体现在以关键材料和器件结构及制备等关键技术突破为核心和重点, 抢抓有机平板显示技术发展的创新机遇和知识产权机遇, 带动我国有机平板显示产业的自主发展.

最近几年, 如何利用不含稀有或贵金属的纯有机材料实现低成本、高内量子效率的荧光OLED成为有机电致发光领域的研究热点, 国内多个单位已经在新一代有机电致发光材料和器件开发上具备了很好的研究基础. 例如, 华南理工大学、清华大学、苏州大学等在开发高性能热活化延迟荧光材料方面取得了许多突破性的成果, 部分光色的关键性能指标达到国际先进甚至领先水平[7~13]. 华南理工大学和吉林大学提出了发光材料的“热激子”新机制[14,15], 吉林大学首次报道了利用共轭自由基的双线态激子发光[16], 清华大学提出了热活化敏化发光机制实现高效率荧光器件的新思路[17], 华南理工大学提出了平面pn异质结型OLED这一结构简单新颖的有机电致发光器件类型[18,19], 这些材料及器件设计思路均有望打破自旋量子统计瓶颈, 实现高效率纯有机发光材料. 这些新一代有机电致发光材料及器件在新型显示技术上有良好的应用前景, 在降低材料成本并实现高性能器件方面具有极大潜力, 同时有望促使我国在新一代电致发光材料与器件领域获得源头创新的知识产权, 占据技术制高点, 实现“换道超车”, 使我国OLED产业长期健康发展.

2 项目研究方向及目标

为了在国际有机电致发光研发和产业化的纷乱格局中占据一席之地, 针对我国OLED显示领域对低成本、高性能材料及简约器件制备工艺等原始创新技术的重大迫切需求, 推进国内OLED科技研发上的源头创新和产业链结构升级, 由华南理工大学作为国家重点研发计划“战略性先进电子材料”重点专项“新型显示”方向中“新一代有机电致发光材料与器件”项目的牵头单位, 联合清华大学、吉林大学、苏州大学、北京大学、武汉大学、浙江大学、陕西师范大学、中国科学院理化技术研究所、中国科学院长春应用化学研究所、中国科学院宁波材料技术与工程研究所、香港城市大学深圳研究院、广州华睿光电材料有限公司、北京鼎材科技有限公司等单位, 提出不含贵重金属的纯有机材料体系及相关器件研究计划. 围绕研发新一代有机电致发光材料和器件的主任务, 充分利用项目团队优势协同攻关, 目标是取得国际认可的原创成果, 发展OLED显示新一代材料, 解决OLED显示材料共性基础科学问题, 在实现指南提出的效率以及寿命关键指标的同时, 推动自主材料的

产业化，满足我国OLED产业的迫切需求．项目共设5个研究方向：(1) 新发光机制的有机发光材料的设计与制备；(2) 热活化延迟荧光机制的有机发光材料的设计与制备；(3) 有机发光材料和器件的稳定性和老化机理研究；(4) 新型发光器件结构和工艺优化设计；(5) 显示器件集成技术与表征评价．这些研究方向分别对应于对推进有机电致发光材料和器件的科技研发和产业化息息相关的5个重要方面．

该国家重点研发计划项目旨在从源头创新和自主知识产权出发，并将研发成果应用和产业化，做到产学研链条的完整衔接．国内对于OLED的研发和产业化推进的投入目前主要集中在面板行业，对于上游的材料研发、器件设计和设备工艺投入相对欠缺．研究方向(1)和(2)旨在攻关上游的材料科学难题，重点研发具有我国自主知识产权的新一代纯有机电致发光材料，在大幅降低材料成本的同时实现高效率OLED器件．新材料新机制也是器件结构创新的重要推动力．此外，研发纯有机电致发光材料对于打破国外技术壁垒的保护具有重大意义，源头上的创新可以为整个后续的OLED产业链的良性发展提供可靠保障．

研究方向(3)针对材料和器件的稳定性开展．在OLED材料和器件真正进入产业化阶段，材料和器件的稳定性成为极其重要的议题．对纯有机化合物而言，材料的化学键强度、在环境因素影响下的化学稳定性以及在电场驱动下分子反复发生氧化还原过程的耐力等因素都极大程度上影响了最终器件的工作寿命和效率滚降，短器件应用寿命严重掣肘OLED发展．研究方向(3)作为材料和器件应用之间重要的纽带，研发成果将直接推进产业化的进程和降低OLED产品的应用成本．长寿命高稳定性OLED材料和器件也可以拓宽OLED在实际中的应用，诸如在严苛条件的环境中OLED显示与照明可以发挥其柔性超薄的优势，为显示与照明行业带来革命性的创新．

研究方向(4)和(5)旨在从器件结构，工艺设计和显示器件集成技术和评估体制上实现自主创新．突破传统理念的器件结构设计，柔性超薄全彩显示的实现和蒸镀工艺与印刷薄膜制备研发将是OLED显示和照明产业化的关键．目前主流的器件结构设计专利同样被国外企业所垄断，如美国UDC(磷光OLED器件)，美国Kodak(经典OLED器件结构专利)等，基于自主开发的新一代纯有机材料，研发新一代有潜力实现高效电致发光的器件结构和工艺是突破国外技术垄断的必经之路．

3 结束语

目前，自主知识产权技术的掌握对提高国家新型显示技术的国际竞争力至关重要．通过国内各大高校、研究单位和企业的优势互补，协同创新，共同推进项目的前进，不仅有利于推进项目成果的商品化，为高新技术企业和研发单位带来经济收益，长远来看，对于国内产业结构升级，推动能源节约和环境保护等方面都具有重大意义．该项目立足于基础科学研发，旨在推进产学研的一体化，使实验室最新高科技成果可以与产业顺利链接，真正革新国内显示和照明行业目前大量依赖国外技术进口和专利购买的老旧格局．

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A new generation of organic light-emitting materials and devices

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Organic light-emitting diodes (OLEDs) have been a research focus for almost 30 years because of their great potential applications in flat-panel displays, solid-state lighting, and wearable electronics. The recombination of holes and electrons within the devices under electrical excitation typically generates 25% singlet excitons and 75% triplet excitons. However, only 25% singlet excitons can be utilized to emit light, and the other 75% triplet excitons are generally wasted through non-radiative transition to give a maximum internal quantum efficiency of about 25% for the first generation fluorescent OLEDs. To improve the internal quantum efficiency, phosphorescent materials have been utilized to exploit the non-radiative triplet state by introducing noble heavy metal atoms like iridium (Ir) and platinum (Pt) to increase spin-orbit interactions. Overall electroluminescence (EL) internal quantum efficiency has been successfully improved to 100% since both singlet and triplet excitons could be harvested due to their radiative triplet excitons and efficient intersystem crossing (ISC) from the singlet excited state to the triplet excited state. Nevertheless, noble metals are indispensable for those phosphorescent materials, which are expensive and nonrenewable. In the past few years, metal-free thermally activated delayed fluorescence (TADF) emitters that can also realize 100% exciton utilization through efficient reverse intersystem crossing (RISC) of triplet excitons are regarded as promising materials for next-generation OLEDs. Besides, the intersystem crossing of excitons between higher energy Tm and Sn with close energy levels may also happen in hybridized local and charge-transfer (HLCT) excited state, where the local excited (LE) state contributes to a high efficiency fluorescence radiative decay, while the charge transfer (CT) state ensures the generation of singlet excitons in high yield through the reverse intersystem crossing from high-lying CT-based triplet excited state back to the CT-based singlet excited state. 75% Non-luminescent triplet excitons can theoretically be transferred to singlet ones via reverse intersystem crossing to give a comparable internal quantum efficiency to that of the phosphorescent devices. In addition, an organic open-shell molecule with one unpaired electron in the highest singly occupied molecular orbital (SOMO) could also be used as an emitter to circumvent the transition problem of triplet. Intermixing of electron-donating and electron-accepting molecules as an emitting layer could also break the fluorescence internal quantum efficiency limit of 25% by using the high reverse intersystem crossing efficiency of the intermolecular excited state (that is, exciplex state). Most recently, a simple strategy towards high-performance fluorescent OLEDs was reported by stacking p-type hole-transport layer and n-type electron-transport layer, resulting in a planar pn heterojunction configuration similar to their inorganic counterparts, namely light emitting diodes (LEDs). Like this, there is a great and urgent demand for low-cost high-performance light-emitting materials, simple device structure and simple manufacturing process in the field of OLED display. This project will focus on the development of noble metal free organic light-emitting materials and their high performance devices, including development of a new generation of organic light-emitting materials and corresponding host materials with high efficiency and practical lifetimes, investigation of their light emitting mechanisms, structure-property relationships, excited states and their regulation processes, etc. Based on the developed materials and devices, full-color OLED display panels will also be designed and developed.

organic light-emitting diodes, organic light-emitting materials, excited state, stability, display panel

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