

稀土掺杂上转换发光材料的研究进展

贾松, 王雪飞*, 史祎诗

中国科学院大学 化学学院, 北京 101408

摘要: 上转换发光, 一种呈现反斯托克斯位移特性的发光现象, 主要通过稀土元素制备的材料来实现。本文深入探讨了稀土掺杂上转换材料的发光机理, 概述了常用的制备技术, 并全面评述了其在生物医学、防伪技术、信息存储等多个领域的现有应用, 同时展望了其在工程领域的潜在应用前景。尽管上转换发光纳米材料在功能多样性方面表现出远超块状材料的显著优势, 但其合成产率和发光效率仍存在挑战, 处于相对较低水平。逐步攻克这些难题, 将有助于进一步拓宽上转换发光材料的应用领域。

关键词: 稀土; 上转换发光; 发光材料; 掺杂

中图分类号: TB34

文献标识码: A

文章编号: 1674-4969(2024)02-0114-23

引言

稀土元素, 包括 15 种镧系元素以及钪(Sc)和钇(Y), 共计 17 种独特元素。这些元素表现出难以被其他元素所代替的卓越的磁、光、电性能。它们在提升产品性能、优化产品结构、增加科技含量以及推动行业技术进步方面发挥着至关重要的作用。目前, 稀土永磁、发光、储氢、催化等功能材料已成为先进装备制造、新能源、新兴产业等高新技术产业不可或缺

的原材料。由于稀土元素储量稀少, 且在电子、石油化工、冶金、机械、新能源、轻工、环境保护、农业等多个领域发挥着不可替代的作用, 它们已成为越来越重要的战略资源^[1-5]。

在镧系元素的多种价态中, 三价态(Ln^{3+})表现得最为稳定。此时, 这些元素的 4f 轨道处于全空, 半满或全满的状态。正因为镧系元素具有这种特殊的 4f 电子构型, 它们展现出了丰富的离散能级。在这些能级之间发生的光学跃迁能够产生覆盖从近红外、可见

收稿日期: 2023-11-20; 修回日期: 2023-12-05

基金项目: 中央高校基本科研业务费; 北京市自然科学基金(8222074)

作者简介: 贾松 (2000—), 男, 硕士研究生, 研究方向为稀土上转换发光及其色彩调制。

*王雪飞 (1978—), 男, 博士, 副教授, 研究方向为现代光谱检测技术和大气有色碳成因和检测。

E-mail: wangxf@ucas.ac.cn(通讯作者)

史祎诗 (1981—), 男, 博士, 教授, 研究方向为光电信息处理的理论、技术、工程。

引用格式: 贾松, 王雪飞, 史祎诗. 稀土掺杂上转换发光材料的研究进展[J]. 工程研究——跨学科视野中的工程, 2024, 16(2): 114-136. DOI: 10.3724/j.issn.1674-4969.20230004

Jia Song, Wang Xuefei, Shi Yishi. Research Progress of Rare Earth Doped Upconversion Luminescent Materials[J]. Journal of Engineering Studies, 2024, 16(2): 114-136. DOI: 10.3724/j.issn.1674-4969.20230004

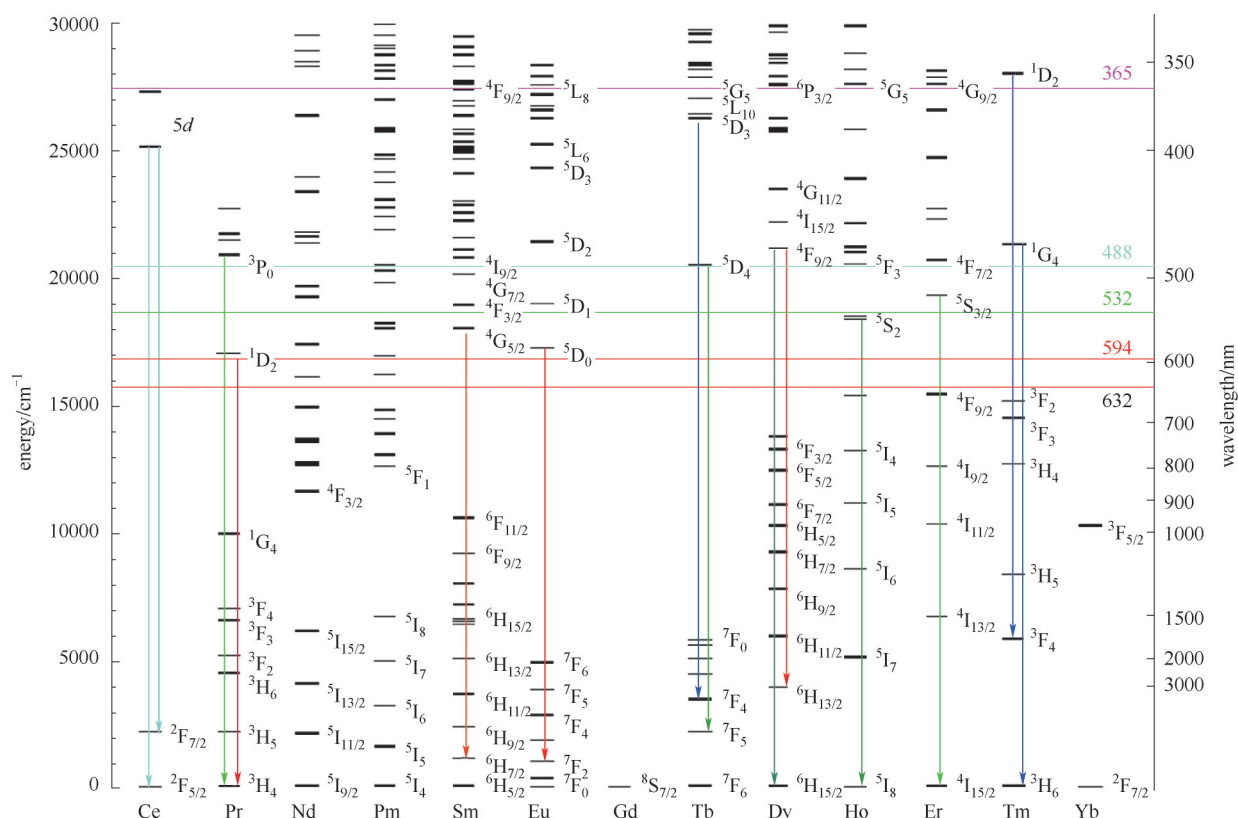


图1 在硅酸盐玻璃中观察到的具有主要可见发射跃迁的三价稀土离子的能级图, 用箭头表示荧光的近似颜色。横过图的水平线表示用波长(nm)标记的常见有机标签激发源的位置。用365 nm谱线激发稀土离子^[6]

Figure 1 Energy level diagram of trivalent RE ions with dominant visible emission transitions observed in silicate glasses designated by arrows representing the approximate color of the fluorescence. Horizontal lines extending across the diagram designate the location of common organic label excitation sources labeled by wavelength in nm. The 365-nm line was used to excite the RE ions^[6]

光区到紫外光区的广泛发射(如图1所示)^[6-8]。不仅如此, 与有机染料相比, 镧系元素的发射谱线更加尖锐, 从而赋予了它们极高的色光纯度。此外, 这些镧系掺杂的上转换发光材料还具备出色的抗光漂白性能、超大的 Stokes 位移以及良好的生物相容性等特点。这些优势是有机染料、量子点等其他发光材料所无法比拟的^[9-14]。

稀土离子的能级结构通常呈现阶梯状排列, 其激发态具有较长的寿命, 这一特性使得它们成为制备上转换发光材料的理想选择。早在 1959 年, 物理学家 Bloembergen^[15]就提出了上转换发光的概念, 即通过低能量光子的激发获得高能量光子的发射, 从而实现反 Stokes 发光。近年来, 随着纳米科学和纳米技术的迅猛进步, 稀土上转换材料已经历了从较大尺度到纳米尺度的演变。在纳米尺度上的精细调控进一步丰富

了上转换材料的功能性, 使其在生物医学^[16-21]、光学传感^[22-35]、显示器件^[36-41]等领域的应用日益凸显。例如, 利用稀土上转换发光材料发光波长可调的特性, 可以实现多种生物分子的同时成像。此外, 通过将药物与稀土上转换发光材料结合, 借助外部激发, 便可控制药物的释放, 进而达到精准治疗的目的。

上转换发光是一种特殊的发光现象, 它没有遵守斯托克斯位移规律, 即吸收低能量的光子却能发射出较高能量的光子, 两者之间的能量差被称为斯托克斯位移^[42-43]。典型的上转换材料通常由三部分构成: 基质、敏化剂和激活剂。基质虽然不直接参与发光过程, 但它为敏化剂和激活剂提供了一个稳定的晶格环境, 并且对效果产生着重要影响。不同的晶体结构会导致发光的差异性。常见的基质材料包括氧化物、氟化物和硫化物等, 其中氟化物具有较低的声子能量因

此有较高的发光效率从而备受青睐^[44-50]。敏化剂在上转换过程中扮演着能量传递的角色, 它将吸收到的激发光能量有效地传递给激活剂。常见的敏化剂有 Nd^{3+} 和 Yb^{3+} 离子, 它们分别能够吸收 808 和 980 nm 波长激光的能量。而激活剂则是上转换体系中的核心发光组分。在接收到来自敏化剂或直接从激发光中吸收的多个光子能量后, 激活剂离子会跃迁至较高的能级, 随后通过辐射跃迁的方式回到基态并释放出光能。最常用的激活剂包括 Er^{3+} 、 Ho^{3+} 和 Tm^{3+} 。其中, Er^{3+} 和 Ho^{3+} 是优秀的红光/绿光发射离子, 而 Tm^{3+} 则是出色的蓝光/紫外光发射离子。

常见的上转换发光方式有四种(图2), 分别是(1)同时双光子吸收(two-photon absorption, TPA), 即发光材料在极短时间内同时捕获两个光子跃迁至激发态, 随后释放出一个光子的过程;(2)激发态吸收(excited state absorption, ESA), 指材料在吸收一个光子达到中

间能级后, 在该电子返回基态之前再吸收一个光子跃迁至更高能级, 最终以辐射跃迁的形式回到基态。此过程可吸收多个光子, 但须满足能级差与激发光能量匹配的条件, 例如 Er^{3+} 离子可以通过吸收两个 980 nm 的光子实现 650/540 nm 的辐射, 而以 1534 nm 波长的激光作为激发光源时则需要更多的光子;(3)能量传递上转换(energy transfer upconversion, ETU), 该过程涉及到两个或多个离子之间的能量传递, 在最简单的两个离子模型中, 一个离子在激发光的泵浦下跃迁到激发态, 随后将能量传递给另一个离子后以无辐射跃迁的方式回到基态, 若这个能量传递给同种离子则称为能量迁移(energy migration, EM), 传递给不同的离子则称为能量传递(energy transfer, ET)。若两种不同的离子激发态能量接近, 则可以通过快速的共振能量传递(resonant energy transfer, RET)将另一离子泵浦到激发态。若两种离子的激发态能级不匹配, 则需要通

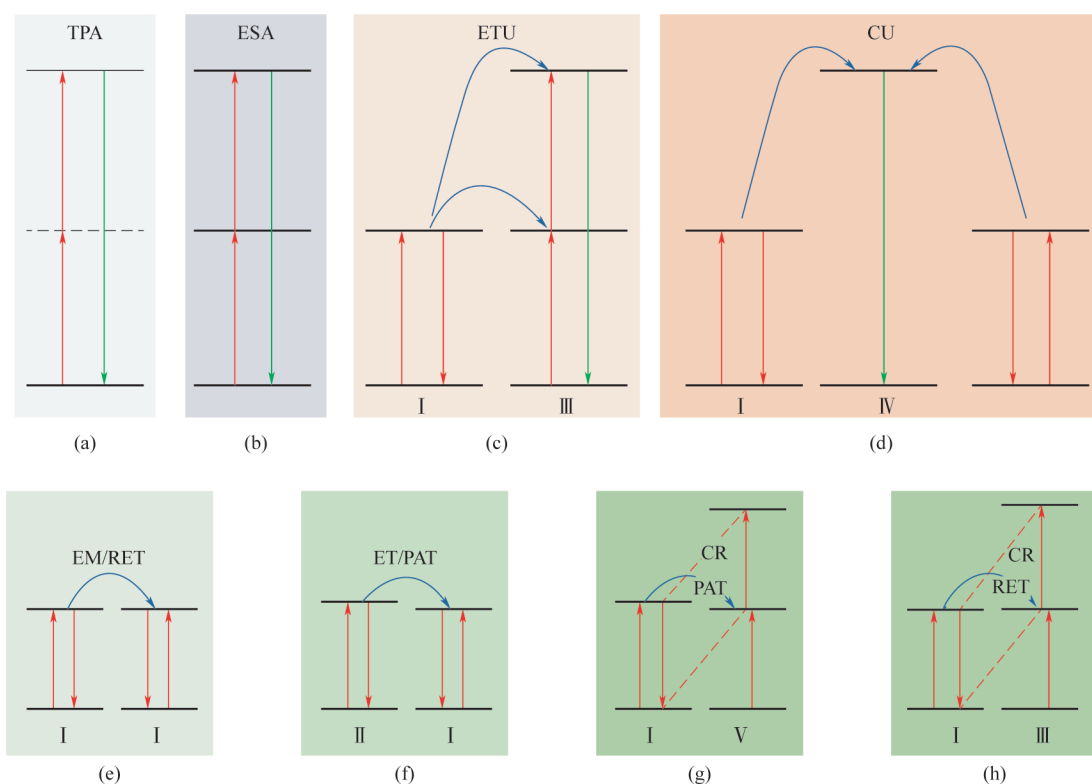


图2 上转换过程示意图[(a)~(d)]; 发生在相同或不同离子之间能量传递过程的示意图[(e)~(h)]。向上(红色)和向下(绿色)的全箭头分别代表直接激发过程和发射过程, 蓝色的箭头表示能量传递过程; I、II、III、IV、V代表不同的离子

Figure 2 Schematic diagrams of upconversion processes [(a)~(d)]; Schematic diagrams of energy transfer processes occurring between the same or different ions [(e)~(h)]. Upward (red) and downward (green) full arrows represent direct excitation and emission processes, respectively, while blue arrows indicate energy transfer processes; I、II、III、IV、V represent different ions

过声子辅助能量传递(phonon-assisted energy transfer, PAT)过程将能量传递给另一离子, 要使另一离子从中间态到达更高的能级则需要通过可逆的交叉弛豫(cross-relaxation, CR)过程实现。例如 Yb^{3+} 离子敏化 Tm^{3+} 离子到更高能级的过程。在实际的研究中, 交叉弛豫多指发生在同种激发态离子之间的, 部分激发能参与的能量传递过程, 一般认为交叉弛豫是有害的会导致荧光的猝灭, 并且当掺杂浓度较高时才能观察到明显的交叉弛豫现象; (4)合作上转换(cooperative upconversion, CU), 即两个离子在被激发光泵浦到激发态后同时将能量传递给另一种离子, 将其泵浦到激发态后以辐射跃迁的形式跃迁到基态发光。这种离子的激发态和基态之间的能级差比较大且不存在寿命较长的中间态能级, 单个离子的能量不足以将其泵浦到激发态, 只有两个或多个离子合作才可以将其泵浦到激发态。因此这种上转换体系发光效率较低。ETU是最常见的上转换发光机制, 通过改变掺杂浓度就可以显著的改变这一过程的效率。这四种上转换的过程展示在图 2(a)~(d), 能量传递过程则展示在图 2(e)~(h)。

除了上述的四种上转换过程以外, 光子雪崩(photon avalanche, PA)也是一种上转换发光的方式, 但是这种现象在纳米材料中并不常见, 并且该过程依赖于泵浦光能量, 且对激发响应迟缓^[51-54]。除此之外, 还有一种十分重要的机制为能量迁移介导上转换(energy migration-mediated upconversion, EMU)。2011年, Wang 等^[55]报道了能量迁移介导上转换(EMU)过

程[图 3(a)]。在这个核壳系统中 Gd^{3+} 离子被选作构造上转换纳米颗粒的基质以实现界面间的能量迁移。具体的过程如下: Yb^{3+} 离子吸收 980 nm 波长激光的能量, 并将能量传递给 Tm^{3+} 离子, 使 Tm^{3+} 实现上转换发光, 并且将高能态的能量传递给 Gd^{3+} 离子($^1\text{I}_6 \rightarrow ^6\text{P}_{7/2}$), 随后通过 Gd^{3+} 离子之间的能量迁移将激发能从核中传递到壳层中, 使壳层中如 Eu^{3+} 、 Tb^{3+} 、 Sm^{3+} 、 Dy^{3+} 等难以通过能量传递上转换等方式实现上转换发射的离子发光。除此之外, 该课题组^[56]还在 2015 年报道了另一种相似的以 Tb^{3+} 离子介导的界面能量传递过程并且成功观察到壳层中 Eu^{3+} 离子的发光[图 3(b)]。这样的核壳之间的能量传递拓展了发光中心的种类, 并且通过不同激活剂的组合、掺杂比例的调整, 从而实现白色或多色发射调谐。

1 稀土上转换发光材料的合成

常见的上转换材料合成方法有: 共沉淀法^[57-61]、水热法^[51,62-65]、高温热解法^[66-71]等。利用这些方法, 可以合成出从纳米到微米尺度的材料。尽管块状的上转换发光材料在发光效率方面表现最佳, 但随着纳米科学的不断发展以及生物医学和光学领域的需求日益增长, 构建尺寸均匀、形貌统一且功能多样的上转换纳米颗粒(upconversion nanoparticles, UCNPs)已成为当下的研究重点。鉴于前文所提及的各类基质中, 氟化物因其较低的声子能量而展现出优越的上转换发光性能, 所以本文将着重介绍采用共沉淀法制备上转换纳

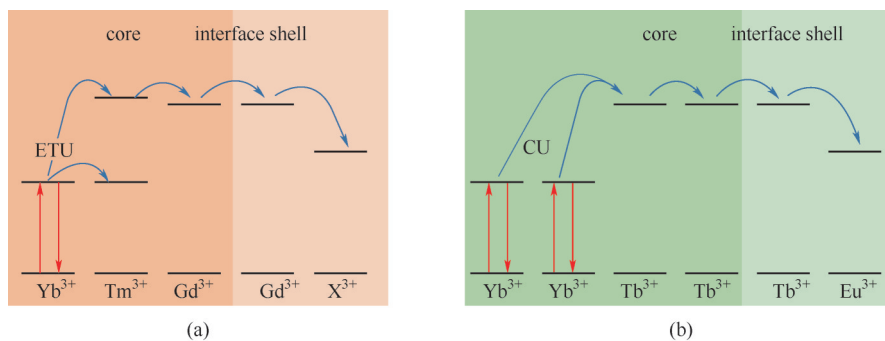


图3 通过核壳结构实现的 Gd^{3+} 离子亚晶格介导的能量迁移光子上转换(a); 通过核壳结构实现的 Tb^{3+} 离子介导的界面能量传递光子上转换(b)

Figure 3 Photon upconversion through the Gd^{3+} ions sublattice-mediated energy migration by a core-shell structure (a); Photon upconversion through the Tb^{3+} mediated interfacial energy transfer by a core-shell structure (b)

米颗粒的方法。

1.1 水热法

水热法是为常用的合成无机材料的方法。2004年Heer等^[62]报道了通过水热法合成Yb-Er或Yb-Tm掺杂的 NaYF_4 纳米颗粒。通过此方法合成的纳米颗粒粒径分布在5~30 nm之间, 并且提出了可以通过继续包覆 NaYF_4 壳层的方式来继续增加上转换发光效率。通过这样的方法合成出的纳米颗粒是 α 相的, 2005年Li等^[63]提出了一种改进后的水热法可以合成出发光效率更高的 β 相的纳米颗粒。并且通过选择不同的表面活性剂控制纳米颗粒的形貌, 如CTAB会使纳米颗粒生长成棒状, EDTA则会使纳米颗粒呈现为球状。

1.2 共沉淀法

而共沉淀法(co-precipitation)操作简单并且容易控制纳米颗粒的尺寸和形貌, 可以用来合成 LnF_3 、 MLnF_4 型上转换纳米颗粒, 因此目前被广泛应用。Gnanasammandhan等^[72]详细地描述了一种通过共沉淀法合成以 NaYF_4 为基质的上转换纳米晶的方法。即使用油酸作为配体, 1-十八烯作为溶剂, 在油酸和稀土离子形成配合物后, 向反应体系中加入含 Na^+ 、 F^-

离子的沉淀剂, 在随后的升温以及保温过程中逐渐生成上转换纳米晶。这种方法可以制备尺寸非常均匀的 NaYF_4 纳米颗粒。图4为完整的合成与纯化周期的实拍图。

Wang等^[73]也详细地阐述了利用共沉淀法制备 NaGdF_4 纳米颗粒的流程, 并介绍了基于此方法合成核-壳结构纳米颗粒的技术。这两类纳米颗粒的核心制备步骤相似, 可概括为三个主要环节: 配合物的生成→共沉淀过程→结晶成核。在共沉淀步骤中, 形成的相对较大的晶核成为晶体生长的“种子”。在高温保温阶段, 小尺寸的纳米颗粒溶解后, 会继续在这些较大尺寸的纳米晶体上生长, 这一过程被称为奥斯特瓦尔德熟化(Ostwald ripening)^[74]。而核壳结构纳米颗粒的合成则是通过引入前驱体, 即经过纯化的纳米晶作为种子, 从而形成核壳结构(如图5所示)。图6则展示了典型的通过共沉淀法合成的核或核-壳结构纳米颗粒的形貌。此外, 共沉淀法还可以推广到以其他稀土离子($\text{Ln}=\text{Tb}^{3+}$, Lu^{3+} , Eu^{3+} ...)和其他阳离子($\text{M}=\text{Li}^+$, K^+ , Ca^{2+} , Mg^{2+} ...)构成的上转换纳米晶。

核壳结构的形成可以通过种子介导的逐层外延生长法来实现, 但这种方法如前文所述, 适合生长单层活性/惰性壳, 对于多层核壳的包覆则显得步骤繁多、合成周期长且操作繁琐。为了解决这个问题, Li

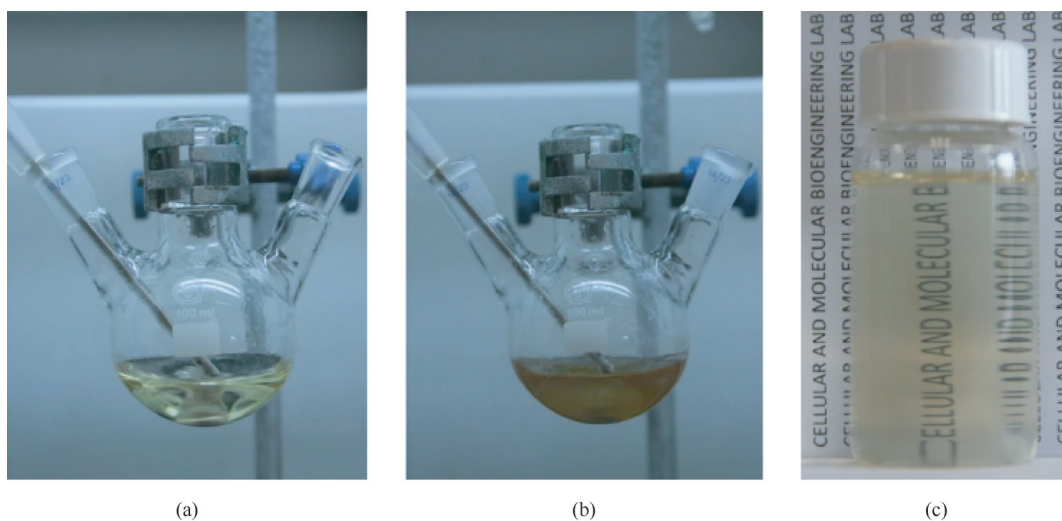


图4 油酸与1-十八烯的镧系元素油酸配合物(a); 在300°C孵育1 h后(b); 洗涤后分散在环己烷中的上转换纳米颗粒(c)^[72]

Figure 4 Lanthanide oleate complexes of oleic acid and 1-octadecene (a); After incubation at 300°C for 1 hour (b); Upconversion nanoparticles dispersed in hexane after washing (c)^[72]

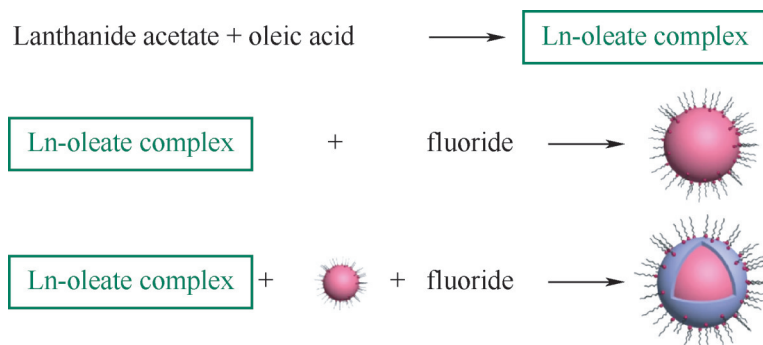


图5 共沉淀法合成镧系元素掺杂的 NaGdF_4 及其核壳纳米晶体示意图^[73]

Figure 5 Schematic illustration of the co-precipitation strategy for the synthesis of lanthanide-doped NaGdF_4 and its core-shell nanocrystals^[73]

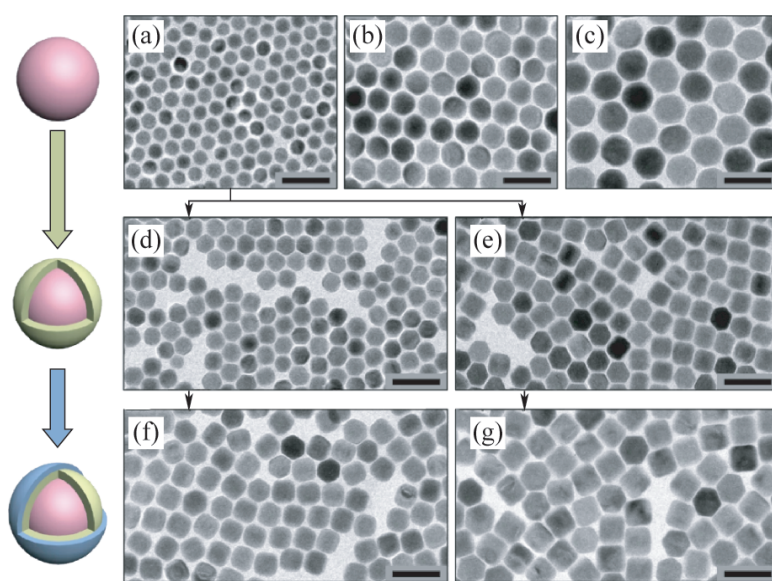


图6 NaGdF_4 纳米晶体的尺寸调控。分别加入 3.3 (a)、3.1 (b) 和 2.7 ml (c) NH_4F /甲醇溶液制备的 $\text{NaGdF}_4:\text{Yb}, \text{Tm}$ 纳米晶体的 TEM 图像。分别加入 50 (d) 和 25 (e) mg 15 nm 核粒子制备的 $\text{NaGdF}_4:\text{Yb}, \text{Tm}@\text{NaGdF}_4:\text{Tb}$ 核壳纳米晶体的 TEM 图像。分别以 [(d)、(e)] 核-壳纳米晶体为种子, $\text{Gd}(\text{CH}_3\text{CO}_2)_3$ 原液为壳前驱体, 按照惰性壳层包覆工艺制备的 $\text{NaGdF}_4:\text{Yb}, \text{Tm}@\text{NaGdF}_4:\text{Tb}@\text{NaGdF}_4$ 核-壳-壳纳米晶体的 TEM 图像 [(f)、(g)] (比例尺为 50 nm)^[73]

Figure 6 Size-tuning of the NaGdF_4 nanocrystals. TEM images of $\text{NaGdF}_4:\text{Yb}, \text{Tm}$ nanocrystals prepared by adding 3.3 (a), 3.1 (b) and 2.7 ml (c) of NH_4F /methanol solutions, respectively. TEM images of $\text{NaGdF}_4:\text{Yb}, \text{Tm}@\text{NaGdF}_4:\text{Tb}$ core-shell nanocrystals prepared by adding 50 (d) and 25 (e) mg of 15 nm core particles. Using core-shell nanocrystals in [(d), (e)] as seeds and $\text{Gd}(\text{CH}_3\text{CO}_2)_3$ stock solution as the shell precursor, $\text{NaGdF}_4:\text{Yb}, \text{Tm}@\text{NaGdF}_4:\text{Tb}@\text{NaGdF}_4$ core-shell-shell nanocrystals were prepared according to the inner shell coating process, and the TEM images are (f) and (g) (scale bar: 50 nm)^[73]

等^[74]提出了一种新颖的方法: 一锅法连续逐层包覆法(one pot successive layer-by-layer strategy, SLBL)(图 7)。这种方法极大地简化了多层核壳包覆的工序, 提高了合成效率。同时, 该方法还可以通过控制前驱体的注入量和保温时间来精确调控壳层的厚度, 实现从单个壳层(~ 0.36 nm)到超过二十个壳层(~ 8 nm)的均匀包覆。更高质量、更均匀的外壳不仅提升了上转换纳

米颗粒的发光效率, 还使得功能丰富的高集成度核-多壳纳米颗粒的合成变得更加简单和可控。更进一步的是, Johnson 等^[75]通过改变前驱体的注入速度来控制外延生长的 NaYF_4 壳层是 α 相还是 β 相。他们还比较了这两种分别包覆了各向同性(α - NaYF_4)和各向异性壳(β - NaYF_4)的纳米颗粒的发光寿命和绝对量子产率。这一发现为上转换纳米颗粒的合成和性能调控提

供了新的思路和方法,有助于推动上转换材料在生物医学、光学等领域的应用发展。

2 稀土发光材料的应用

上转换纳米颗粒因其独特的性质在多个领域展现了广阔的应用前景。其中,低毒性是其备受关注的特点之一,这一特性使其在生命科学领域得到了广泛应用。例如,在检测传感方面,上转换纳米颗粒可以用于生物分子的高灵敏检测,为生物医学研究提供了有力工具。在光动力治疗方面,它们可以作为光敏剂的载体,将光能转化为化学能,从而实现了对癌细胞的精确杀灭。此外,在活体成像领域,上转换纳米颗粒的发光性能使其能够实现对生物体内微观结构和生理过程的可视化观察^[76-82]。除了生命科学领域,上转换纳米颗粒的抗光漂白性质也使其在高等级防伪和信息储存等领域得到了广泛应用。在防伪领域,利用上转换纳米颗粒的发光特性可以制作出难以伪造的防伪标签或图案。在信息储存方面,上转换纳米颗粒的多层核壳结构和可调谐发光性能为实现高密度、高安全性的数据存储提供了可能^[83-89]。

2.1 生物应用

上转换发光是一种反斯托克斯位移的发光,当使用近红外光源作为激发源时几乎可以完全避免生物体产生自体荧光。此外,上转换发光和激发光都处于生物组织的光学透明窗口内时,才能使得信号有更深的穿透深度。例如, Er^{3+} 离子的上转换发光光谱中,红光($\sim 650\text{ nm}$)的穿透深度显然大于绿光($\sim 540\text{ nm}$)的穿

透深度。然而,低浓度掺杂 Er^{3+} 的纳米颗粒的发光以绿光为主,但增加掺杂浓度会导致发光猝灭,降低发光效率。2011年,Wang等^[90]报道了一种以 Mn^{2+} 为基质的纳米颗粒 $\text{KMnF}_3:\text{Yb},\text{Er}$ 。其中 Er^{3+} 离子的绿光发射完全消失,取而代之的是强烈的红光发射。随后他们将这种纳米颗粒与以 Y^{3+} 离子做基质的颗粒对比,其强烈的红光发射可以穿透更深的猪肉组织。传统的 $\text{NaYF}_4:\text{Yb},\text{Er}$ 纳米颗粒在增加 Yb^{3+} 离子的掺杂浓度后红光发射增强,绿光发射相对减弱。但相较于 $\text{KMnF}_3:\text{Yb},\text{Er}$ 而言,红光的发光强度较弱,因此相同厚度的猪肉组织得到的信号也偏弱(图8)^[90]。

2012年,Gu等^[91]开发了另一种 Mn^{2+} 掺杂的 $\text{NaYF}_4:\text{Yb},\text{Er},\text{Mn}$ 纳米颗粒,并将其成功应用于小鼠活体成像。如图9(a)~(c)所示,为小鼠注射 $100\text{ }\mu\text{l}$, 2.0 mg 的PEG-UCNPs(PEG交联的上转换纳米颗粒以增加其水溶性),注射深度约为 10 mm 。通过数码相机拍摄的照片可知,这些强烈的红光可以穿透这些组织。图9(d)~(f)展示了当PEG-UCNPs的浓度降低到 0.5 mg 时依然能观察到红光发射。图9(g)~(i)则展示了当注射深度增加到 15 mm 时观察到的红光发射。在2012年以前,很少有穿透深度超过 10 mm 的上转换发光成像的报道。

值得注意的是,尽管红光具备较好的穿透力,但在对深层组织进行成像时,上转换发光的穿透深度仍显不足。近年来,基于近红外二区(NIR-IIb)的成像技术得到了迅猛发展。在这一波长范围($1500\sim 1700\text{ nm}$)内,不仅可以有效减少光散射和自体荧光的影响,还能避开生物组织中水的吸收峰,从而实现亚厘米级的成像深度,并且分辨率也提高到了微米级

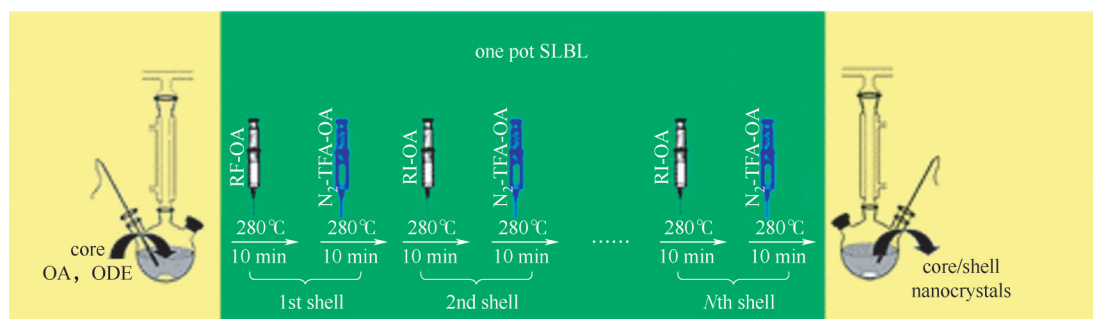


图7 核/壳结构上转换纳米颗粒的SLBL合成程序^[74]

Figure 7 SLBL synthetic procedure for the Core/Shell UCNPs^[74]

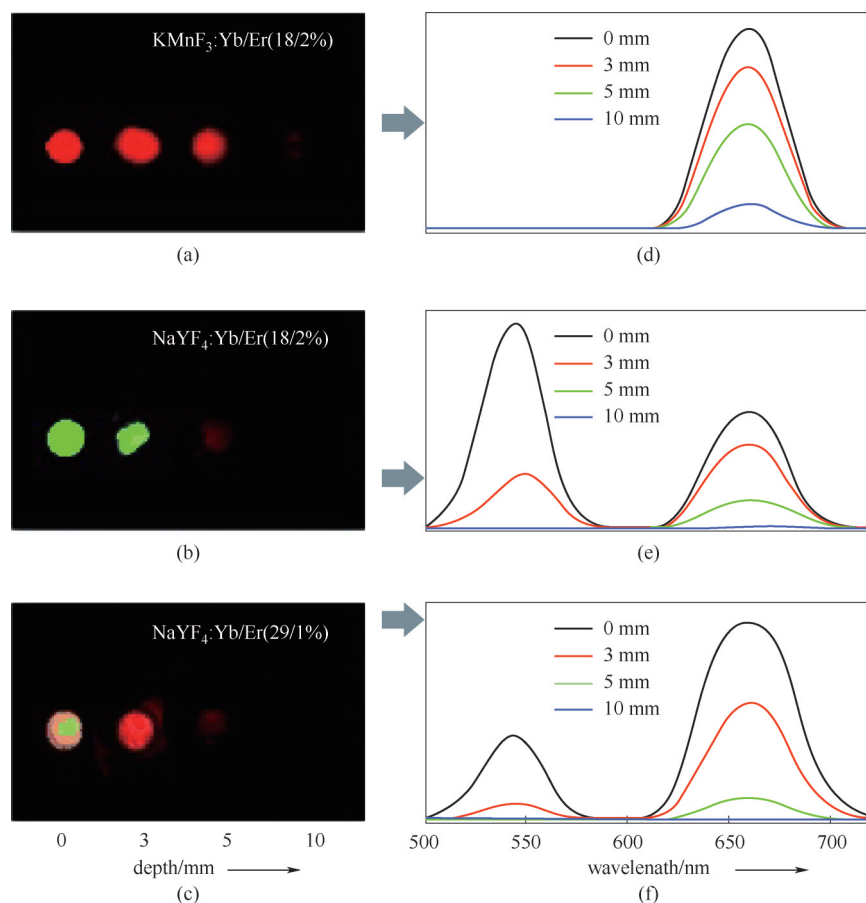


图8 注射不同上转换纳米晶体的猪肉肌肉组织发光图像[(a)~(c)]和对应的发光光谱[(d)~(f)]。所有图像和光谱均在980 nm激光激发下拍摄,功率密度约为 $0.2 \text{ W} \cdot \text{cm}^{-2}$ 。两种体系在0 mm处的发射强度几乎相同^[90]

Figure 8 Luminescence images [(a)~(c)] of porcine muscle tissue injected with different upconversion nanocrystals and the corresponding emission luminescence spectra [(d)~(f)]. All images and spectra were taken under a 980 nm laser excitation with a power density of approximately $0.2 \text{ W} \cdot \text{cm}^{-2}$. Note that the intensities of the two systems at 0 mm are almost the same^[90]

别。此外,稀土离子的下转换发光是斯托克斯位移发光,理论上应具有比上转换发光更高的发光效率。图9展示了在近红外二区窗口中归一化后的稀土离子的发射峰^[92]。其中 Tm^{3+} , Er^{3+} 离子均具有较长的发射波长,以这两种离子为下转换激活剂的纳米颗粒也已被广泛报道。

2017年, Zhong等^[93]报道了一种应用于下转换成像的纳米颗粒: $\text{NaYbF}_4 : \text{Er}$, $\text{Ce}@\text{NaYF}_4$, 其包覆惰性核壳的目的是降低水分子对发光的猝灭。如图11(a)所示^[94], Ce^{3+} 离子的 $^2\text{F}_{5/2}$ 和 $^2\text{F}_{7/2}$ 能级的能级差和 Er^{3+} 离子的 $^4\text{I}_{11/2}$ 和 $^4\text{I}_{13/2}$ 之间的能级差接近,这加速了 $^4\text{I}_{11/2} \rightarrow ^4\text{I}_{13/2}$ 的非辐射弛豫,使得 $^4\text{I}_{13/2}$ 能级被显著填充。与此同时, Er^{3+} 离子的上转换发光显著减弱,而

下转换发光则增强了大约9倍。经过修饰后的纳米颗粒通过尾部静脉注射进入血液循环,经过大约3 s后在小鼠的脑部血管中观察到了下转换发光的信号。这样快速的成像模式还可以推算出小鼠脑部血管的血液流速分布。

2023年, Yang等^[95]报道了一种以 Tm^{3+} 离子为下转换发光中心的核-壳-壳结构上/下转换纳米颗粒: $\text{NaYF}_4 : \text{Yb}$, $\text{Tm}@\text{NaYbF}_4@\text{NaYF}_4$ 并进一步将发光移动到1632 nm(图12)。文中指出 α 相的纳米颗粒上转换发光弱于 β 相,而在近红外区域的下转换发光强度却有了50倍的增强[图12(c)]。随后,他们又利用同样的方法制备出了分别以 Er^{3+} 和 Ho^{3+} 为发光中心的纳米颗粒,将这三种纳米颗粒混合后注入小鼠体内实

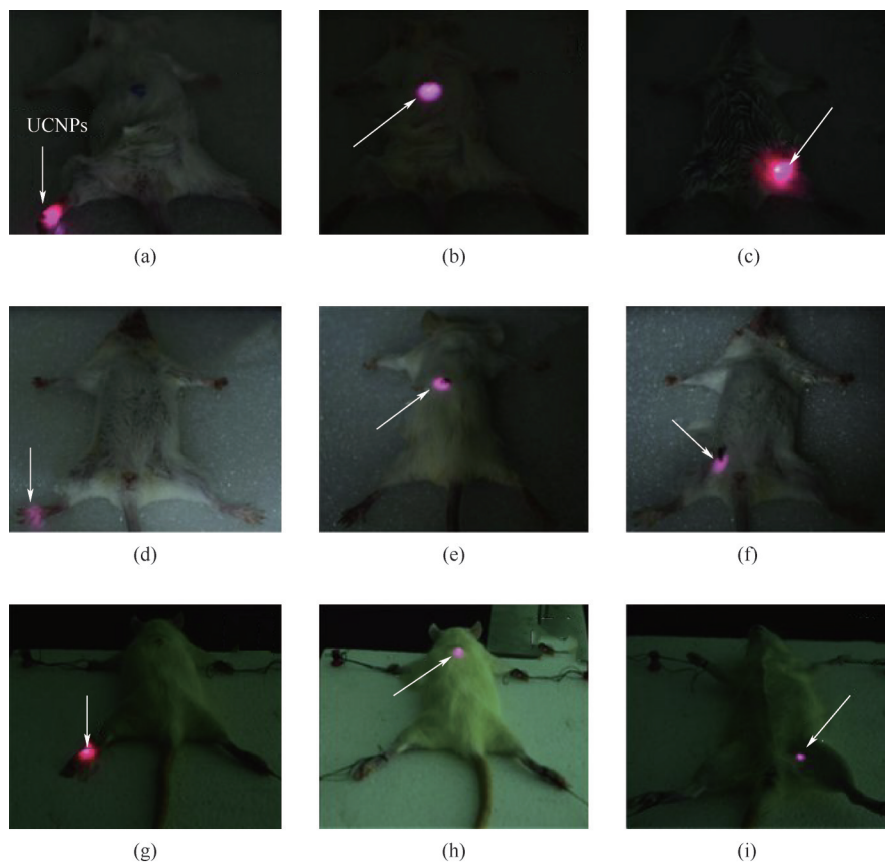


图9 体内上转换发光动物成像研究。将PEG-UCNPs注射到小鼠半透明足部[(a)、(d)、(e)], 背部皮肤下方[(b)、(c)、(e)、(h)]或大腿肌肉[(c)、(f)、(g)]均显示有效发光。(a)~(c)为给药100 μ l 2.0 mg/ml PEG-UCNPs的昆明小鼠;(d)~(f)为给药100 μ l 0.5 mg/ml PEG-UCNPs的昆明小鼠;(g)~(i)为给药100 μ l 2.0 mg/ml PEG-UCNPs的S.D.大鼠^[91]

Figure 9 In vivo upconversion luminescence animal imaging study. PEG-UCNPs were injected into[(a), (d), (e)]translucent foot, [(b), (c), (e), (h)] below skin of back or [(c), (f), (g)] thigh muscles of mice show effective luminescence. (a)—(c) correspond to Kunming mouse with 100 μ l of 2.0 mg/ml PEG-UCNPs; (d)—(f) correspond to Kunming mouse with 100 μ l of 0.5 mg/ml PEG-UCNPs; (g)—(i) correspond to S.D. rat with 100 μ l of 2.0 mg/ml PEG-UCNPs^[91]

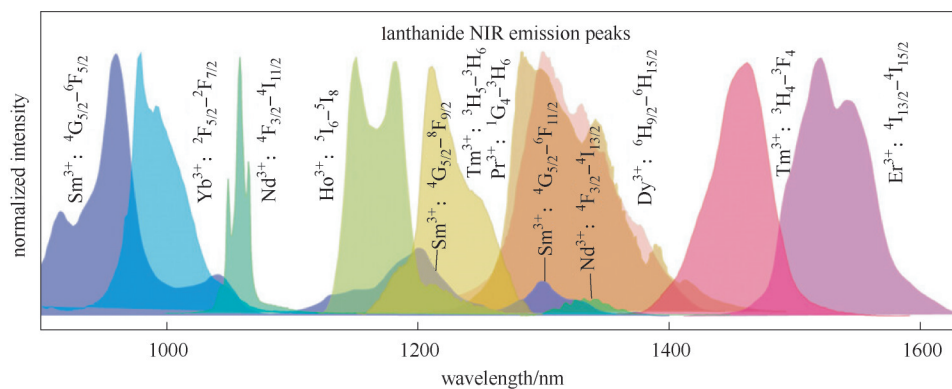


图10 晶体基质中 Sm^{3+} 、 Yb^{3+} 、 Nd^{3+} 、 Ho^{3+} 、 Tm^{3+} 、 Pr^{3+} 、 Dy^{3+} 、 Er^{3+} 等镧系离子的近红外发光光谱^[92]

Figure 10 NIR luminescence spectra of lanthanide ions including Sm^{3+} , Yb^{3+} , Nd^{3+} , Ho^{3+} , Tm^{3+} , Pr^{3+} , Dy^{3+} , and Er^{3+} in crystals hosts^[92]

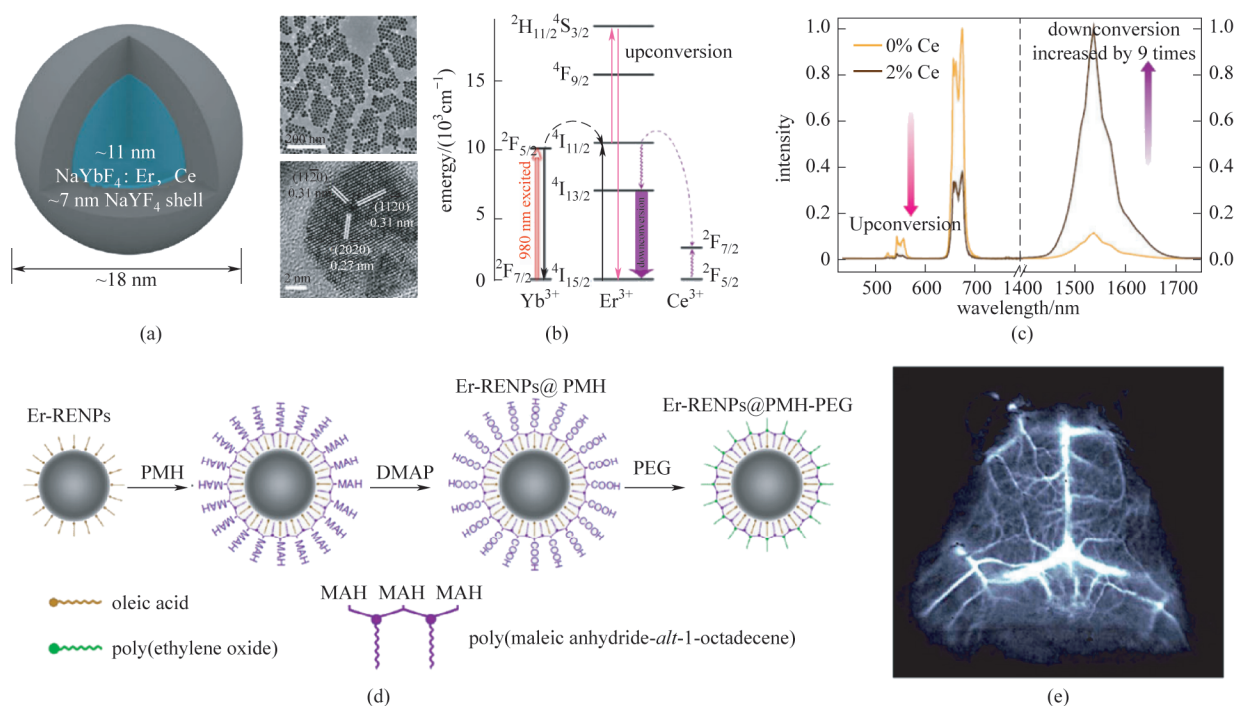


图 11 $\text{NaYbF}_4 : \text{Er, Ce} @ \text{NaYF}_4$ 核壳纳米颗粒(左)示意图及其大尺度 TEM 图像(右上)和 HRTEM 图像(右下)(a); Yb^{3+} 、 Er^{3+} 和 Ce^{3+} 离子之间能量传递的简化能级图(b); 掺杂 0 和 2% Ce^{3+} 的 ErNPs 的上转换和下转换发光光谱(c); ErNPs 的 PMH 包覆和聚乙二醇化过程示意图(d); 静脉注射 ErNPs 后 NIR-IIb 区脑血管图像(曝光时间:20 ms)(e)^[94]

Figure 11 The schematic diagram (left) and large-scale TEM image (right top) and HRTEM image (right bottom) of $\text{NaYbF}_4 : \text{Er, Ce} @ \text{NaYF}_4$ core-shell nanoparticles (a); Simplified energy level diagram for energy transfer between Yb^{3+} , Er^{3+} , and Ce^{3+} ions (b); Upconversion and downconversion luminescence spectra of ErNPs doped with 0 and 2% Ce^{3+} (c); Schematic illustration of the PMH coating and PEGylation process of ErNPs (d); Cerebral vascular images in the NIR-IIb region after intravenous injection of ErNPs (exposure time: 20 ms) (e)^[94]

现了对小鼠脑部的多路复合成像。

相比于更长波长的下转换发光, 上转换发光波长短, 穿透性差, 但上转换发光的能量更高, 是触发光敏剂实现光动力治疗(photodynamic therapy, PDT)的理想光源^[96-100]。将上转换发光和下转换发光通过核壳结构集成在一起有利于更加精准的光动力治疗。Zhao 等^[101]报道了一种通过下转换发光引导的光动力治疗方案。他们首先合成了一种核-4 层壳结构的纳米颗粒(CSNPs), $\text{NaGdF}_4 : \text{Yb, Tm} @ \text{NaGdF}_4 @ \text{NaYbF}_4 : \text{Nd} @ \text{NaGdF}_4 : \text{Yb, Er, Ce} @ \text{NaGdF}_4$ (图 13)。其中上转换发光中心为 Tm^{3+} 离子, 在 980 nm 波长激光的激发下发出 345/450 nm 波长的高能量紫外光以触发光敏剂; 下转换的发光中心为 Er^{3+} 离子, 在 808 nm 波长激光的激发下实现 1550 nm 的近红外光发射。此外, 这些纳米颗粒的表面涂覆了一种 Cy-GSH 染料, 这种染料能够响应谷胱甘肽。在未接触谷胱甘肽之前, 这

种染料会与下转换发光层的敏化层中的 Nd^{3+} 离子竞争吸收 808 nm 的激光, 而不产生发光。在体内循环过程中, 纳米颗粒的近红外二区发射是被关闭的。一旦到达肿瘤部位并接触到谷胱甘肽, 染料便会发生反应, 产生 820 nm 的强发射。这种发射与 Er^{3+} 离子的下转换发光在肿瘤部位和正常部位之间形成了高达 26.9 的信号差异, 从而能够清晰地显示肿瘤位置, 并精确指示光动力治疗应当发生的区域。当激发光切换到 980 nm 后, 即可开始激活上转换发光层, 触发光敏剂进行光动力治疗。

通过核壳结构的构建可以轻易地将上转换和下转换发光中心集合在一起。因此通过下转换发光成像引导上转换发光触发的光动力治疗是未来发展的趋势。但稀土掺杂的上转换发光纳米颗粒的发光效率仍然处在非常低的水平, 还亟待通过优化掺杂比例、核壳结构等方式来提高发光效率, 以增强光动力治疗的实际

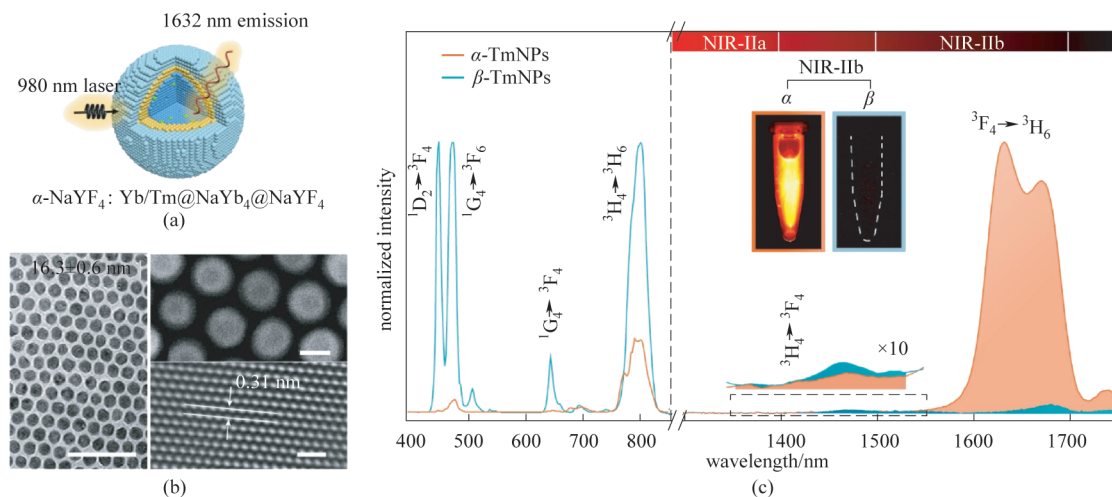


图12 Tm^{3+} 掺杂的立方相核壳结构纳米颗粒示意图(a); 合成 $\alpha\text{-TmNPs}$ 的大尺度TEM图像(比例尺为100 nm), 插图为高角度环形暗场扫描TEM图像(右上, 比例尺为10 nm)和相应的高分辨率图像的快傅立叶变换模式(右下, 比例尺为1 nm)(b); $\alpha\text{-TmNPs}$ 和 $\beta\text{-TmNPs}$ 在980 nm激光激发下的典型发光发射光谱及其在可见光和近红外区的对应强度, 插图为 α -和 β -TmNPs对应的NIR-IIb荧光图像(c)^[95]

Figure 12 Schematic diagram of cubic phase core-shell nanoparticles doped with Tm^{3+} (a); Large-scale TEM image of synthesized $\alpha\text{-TmNPs}$ (scale bar 100 nm), with inset showing high-angle annular dark-field scanning TEM image (right top, scale bar 10 nm) and corresponding fast Fourier transform pattern of the high-resolution image (right bottom, scale bar 1 nm) (b); Typical luminescence emission spectra of $\alpha\text{-TmNPs}$ and $\beta\text{-TmNPs}$ excited by a 980 nm laser, along with their corresponding intensities in the visible and near-infrared regions, with inset showing NIR-IIb fluorescence images of α - and β -TmNPs (c)^[95]

效果, 从而推动其临床应用。

2.2 信息存储和防伪应用

稀土元素因其丰富的能级而能够发出绚丽多彩的光芒, 这些不同颜色的发光可以在不同的条件下被触发, 用于信息存储或防伪^[102-110]。近期, Li等^[111]报道了一种由激发光功率或脉冲光驱动色彩调谐的上转换材料 $\text{Y}_2\text{Mo}_4\text{O}_{15}\text{:40\%Yb}^{3+}, 2\%\text{Ho}^{3+}$ 。这种材料被980 nm波长的连续波激光激发时, 随着功率逐渐升高, 发光的颜色也从红色逐渐变化到黄色和绿色; 而使用980 nm波长的脉冲光激发时, 调整激发光的脉宽也会得到相同的发光色彩转变趋势。这种材料的发光颜色十分丰富, 调制方式也十分丰富, 因此是一种非常好的防伪材料。该研究展示了其在信息加密领域的应用, 采用两种材料配合: $\text{NaYF}_4\text{:40\%Yb}^{3+}, 2\%\text{Ho}^{3+}$ 不具备变色的功能, 只发出绿色光; $\text{Y}_2\text{Mo}_4\text{O}_{15}\text{:40\%Yb}^{3+}, 2\%\text{Ho}^{3+}$ 则可切换红光, 绿光发射。采用ACSII二进制编码: 红色代表1, 绿色代表0。如图14所示, 连续波激光低功率激发时, 所有像素点都发绿光, 降低激发光功率, 部分转变为红光, 此时读

出错误信息“5&7%”[图14(a)]。脉冲光激发时, 所有像素点都发绿光, 增加激发光脉宽, 部分转变为红光, 此时读出错误信息“#cyv”[图14(b)]。而只有当两层信息叠加在一起时, 才能解密真实信息“HENU”[图14(c)]。

Gao等^[112]报道了采用多模持久性发光荧光粉 $\text{Zn}_3\text{Ga}_2\text{GeO}_8\text{:Cr}^{3+}, \text{Yb}^{3+}, \text{Er}^{3+}$ 和 $\text{Zn}_{1.6}\text{Li}_{0.4}\text{GeO}_4\text{:Mn}^{2+}$ 作为发光油墨实现了五模、多色动态防伪。其中, $\text{Zn}_3\text{Ga}_2\text{GeO}_8\text{:Cr}^{3+}, \text{Yb}^{3+}, \text{Er}^{3+}$ 荧光粉表现出光致发光(photoluminescence, PL)、持久发光(persistent luminescence, PersL)、光激发发光(photostimulated luminescence, PSL)、光激发持久发光(photostimulated persistent luminescence, PSPL)和上转换发光(upconversion luminescence, UCL)的五种发光模式, 并且具有丰富的发射颜色。而 $\text{Zn}_{1.6}\text{Li}_{0.4}\text{GeO}_4\text{:Mn}^{2+}$ 荧光粉表现出PL、PersL、PSL和PSPL的四种发光模式, 具有持续较长的可感知的绿色余辉。使用这些多模式持久性荧光粉印制的“蜻蜓上莲”图案显示了在不同发光模式下发射颜色和亮度的动态演变(图15)。

因为稀土离子的发光寿命较长, 通过发光寿命复

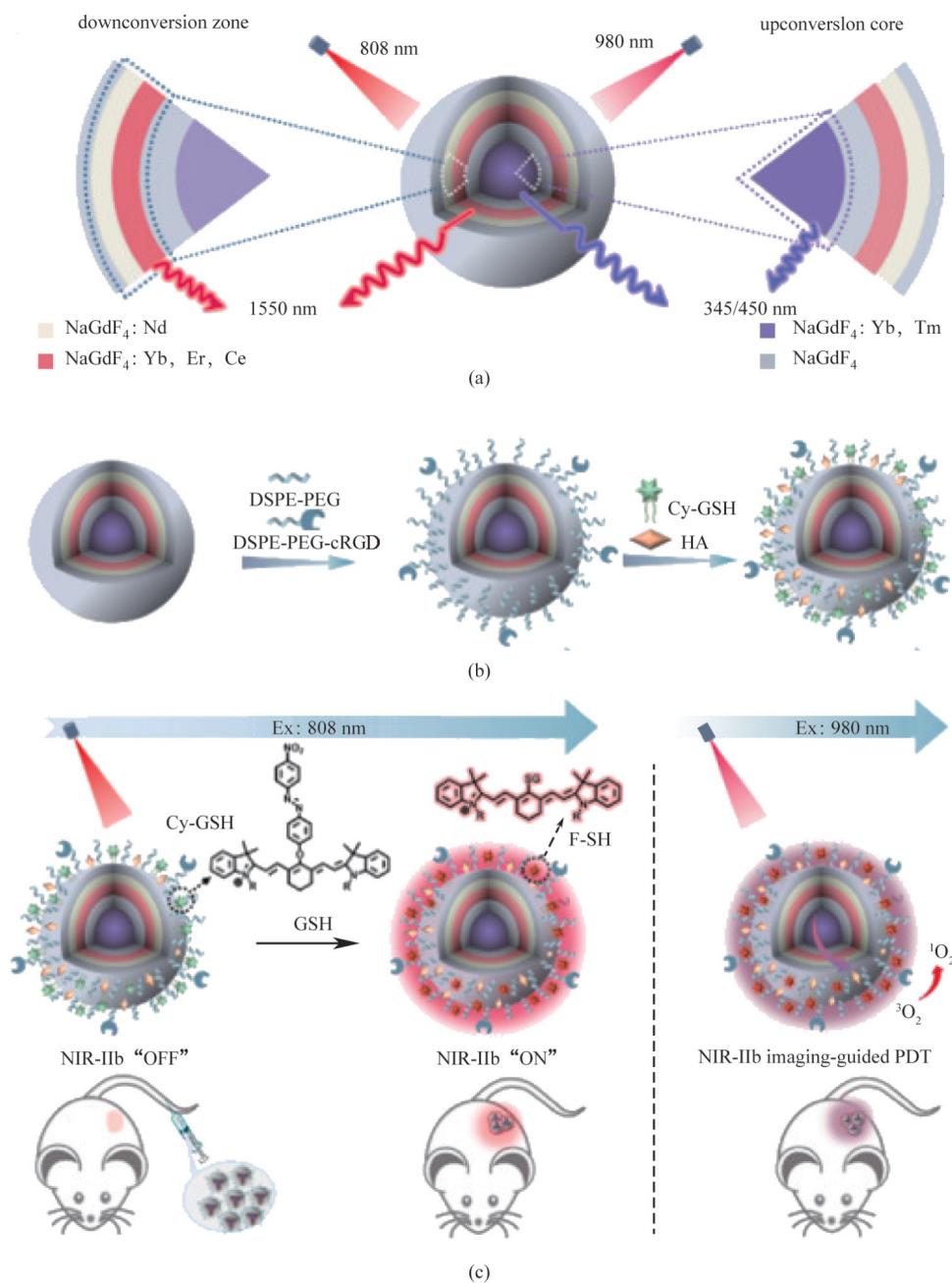


图13 近红外光对体内治疗中CSNPs上下转换辐射的正交激发示意图。CSNP的构建和对应于双近红外激发的上/下转换发射(a); CSNPs-Cy-GSH-HA-cRGD的合成(b)及其在可活化NIR-IIb成像引导PDT中的应用(c)^[101]

Figure 13 Schematic diagram of orthogonal excitation of CSNPs' upconversion and downconversion radiation *in vivo* therapy. The construction of CSNPs and the corresponding up/downconversion emissions upon dual near-infrared excitation (a); The synthesis of CSNPs-Cy-GSH-HA-cRGD (b) and its application in activatable NIR-IIb imaging-guided PDT (c)^[101]

合编码也可以获得高等级的防伪效果。如Lu等^[113]制备了一系列相同Yb³⁺离子掺杂浓度,不同Tm³⁺离子掺杂浓度的上转换纳米颗粒。他们发现不同掺杂的纳

米颗粒具有不同的发光寿命,并且通过控制时间门控装置成像就可以将这些不同寿命的发光区分开。他们将这些上转换纳米颗粒喷墨打印形成相互重叠的照

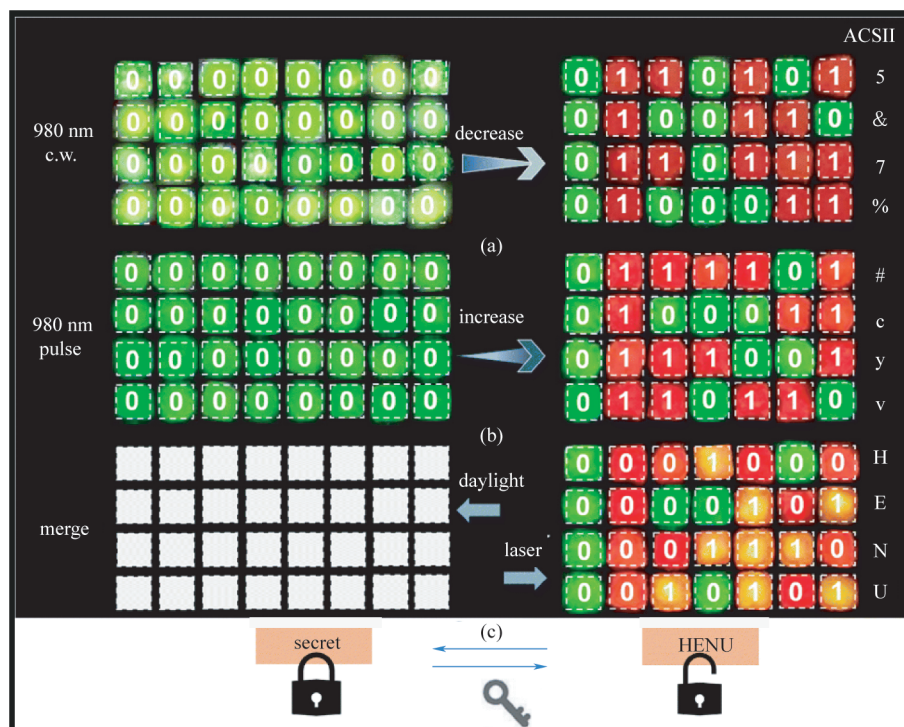


图14 模拟的加密和解密过程。非变色像元用 $\text{NaYF}_4: 40\% \text{Yb}^{3+}, 2\% \text{Ho}^{3+}$ 覆盖, 变色像元用 $\text{Y}_2\text{Mo}_4\text{O}_{15}: 40\% \text{Yb}^{3+}, 2\% \text{Ho}^{3+}$ 覆盖(a)~(b); 把(a)和(b)叠加得到(c)^[111]

Figure 14 Simulated encryption and decryption process. Non-switching pixels are covered with $\text{NaYF}_4: 40\% \text{Yb}^{3+}, 2\% \text{Ho}^{3+}$, while switching pixels are covered with $\text{Y}_2\text{Mo}_4\text{O}_{15}: 40\% \text{Yb}^{3+}, 2\% \text{Ho}^{3+}$ (a)~(b); Overlaying (a) and (b) to obtain (c)^[111]

片, 再通过上述的技术手段就可以将不同的信息区分重建(图16)。

除上述介绍的通过单波长触发的变色或寿命调控来实现防伪或信息存储的方式以外。将不同波长激发的发光层组合在一起, 再通过正交发光的方式来连续地改变发光的颜色并以此来达到防伪或信息存储目的的报道还有很多^[114-118]。但在实际应用中这些多壳层结构的纳米颗粒一般合成路线较为复杂, 相应的激发单元也较为复杂, 所以很难将这些纳米颗粒应用到实际的场景中。因此, 继续开发单波长触发的多色调谐材料是非常有必要的。除了通过交叉弛豫的方式来实现色彩调谐以外, 还需要寻找新的色彩调谐机理。

2.3 工程领域中的潜在应用

光学的测试方式是一种非侵入的测试方式。因为稀土离子的特殊的能级排布, 在上转换发光的过程中, 某些能级的布居受温度影响, 通过建立温度和发

光特性之间的联系即可获得一种非侵入式的温度测量探针。目前为止, 已经有大量的关于上转换发光对温度测量的报道, 且常用 Er^{3+} 或者 Tm^{3+} 离子作为发光中心^[119-123]。Zou等^[124]报道了一种异质结结构的上转换纳米颗粒用于对温度的测量, 测试范围为293~473 K, 分辨率达到了0.26 K。这种特殊的异质结构不仅显著提升了上转换发光的效率, 还为实际工程应用中的测量带来了便利。在化工过程中, 流体的流动是需要重点监测的指标, 在这方面, 上转换纳米颗粒同样展现出了其应用潜力。如Tessitore等^[125]报道了一种纳米颗粒 $\text{NaGdF}_4: 49\% \text{Yb}^{3+}, 1\% \text{Tm}^{3+} @ \text{NaGdF}_4: 20\% \text{Tb}^{3+}$ 。该颗粒利用 Tm^{3+} 离子和 Tb^{3+} 离子之间发光寿命的差异, 以及核壳结构对能量迁移的影响, 通过彩色滤光光学显微镜成像技术, 能够捕捉到不同流速下产生的发光拖尾现象, 从而建立起与流速之间的关联[图17(a)]。这种新方法在速度测试中展现出了相对标准偏差5%或更低的优异性能, 且无需任何校准

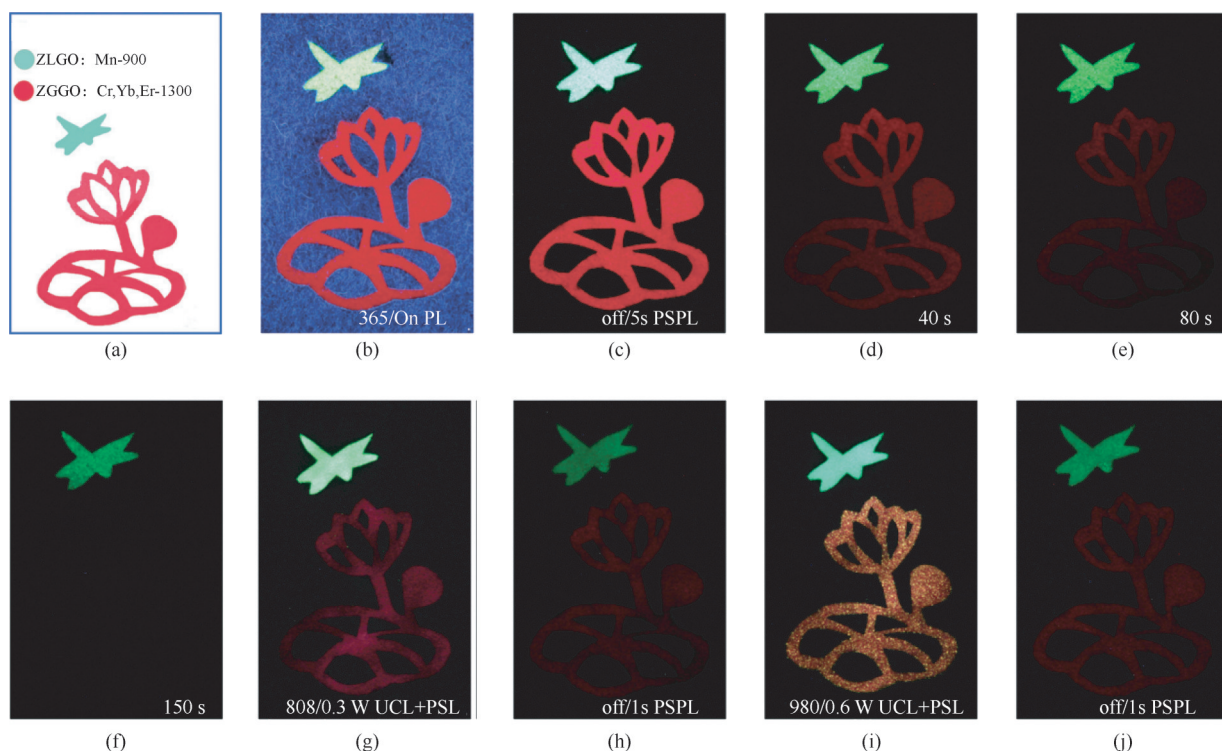


图15 采用ZLGO:Mn-900荧光粉(蜻蜓)和ZGGO:Cr,Yb,Er-1300荧光粉(莲花)印制的五模(PL、PersL、UCL、PSL和PSPL模式)“蜻蜓上莲”图案的数字图像。“蜻蜓上莲”图案的设计(a)。365 nmUV灯照射下(5 min)和照射后的PL和PersL图像[(b)~(f)]。808 nmNIR激光二极管(0.3 W)照射下和照射后的UCL + PSL和PSPL图像[(g)、(h)]。在980 nm近红外激光二极管(0.6 W)照射下和照射后的UCL + PSL和PSPL图像[(i)、(j)]。在蜻蜓和莲花肉眼都看不见后进行UCL + PSL成像。成像参数为manual/ISO 3200/4 s[(b)~(g)、(i)], 成像参数为manual/ISO 3200/15 s[(h)、(j)]^[112]

Figure 15 Digital image of the “dragonfly on lotus” pattern, printed using ZLGO:Mn-900 fluorescent powder (dragonfly) and ZGGO:Cr,Yb,Er-1300 fluorescent powder (lotus), with five modes (PL, PersL, UCL, PSL, and PSPL) is presented. The design of the “dragonfly on lotus” pattern (a). PL and PersL images [(b)~(f)] under 365 nm UV light irradiation (5 min) and after irradiation. UCL + PSL and PSPL images [(g), (h)] under 808 nm NIR laser diode irradiation (0.3 W) and after irradiation. UCL + PSL and PSPL images [(i), (j)] under 980 nm NIR laser diode irradiation (0.6 W) and after irradiation. UCL + PSL imaging was performed after the dragonfly and lotus were rendered invisible to the naked eye. Imaging parameters were manual/ISO 3200/4 s [(b)~(g), (i)], and imaging parameters were manual/ISO 3200/15 s [(h), (j)]^[112]

步骤[图17(b)]。

2022年, Huang等^[126]报道了一种更加简单的通过上转换纳米颗粒对流体速度测量的方法。他们合成了一种具有非稳态色彩调谐性质的纳米颗粒NaYF₄:Yb/Ho/Ce@NaGdF₄,如图18所示,随着流体的速度增加,上转换发光逐渐向绿光移动,由此即可建立发光的颜色和流体流速之间的关系。

此外,地球上的太阳辐照光谱中约有50%是红外能量,这些低能量的光子还未得到十分有效的应用。而稀土上转换材料可以将这些近红外光子转换成可见光或紫外光,这些较高能量的光可被用于光催化等领域。如Gao等^[127]报道了将上转换纳米颗粒和半

导体材料结合后在近红外光的触发下可实现光解水(图19)。类似的将上转换纳米颗粒和半导体材料结合起来利用近红外光的报道还有很多^[128-132]。但上转换材料在此类系统中的作用仅为提供可见-紫外光,通过搭配不同的半导体材料就可以作为不同反应的催化剂,因此此类体系无需过多赘述。目前,该领域发展的瓶颈仍在于上转换发光的效率偏低。

3 结论与展望

上转换发光材料凭借其高稳定性、低毒性及良好生物相容性等优势,在多个领域展现出巨大的应用潜

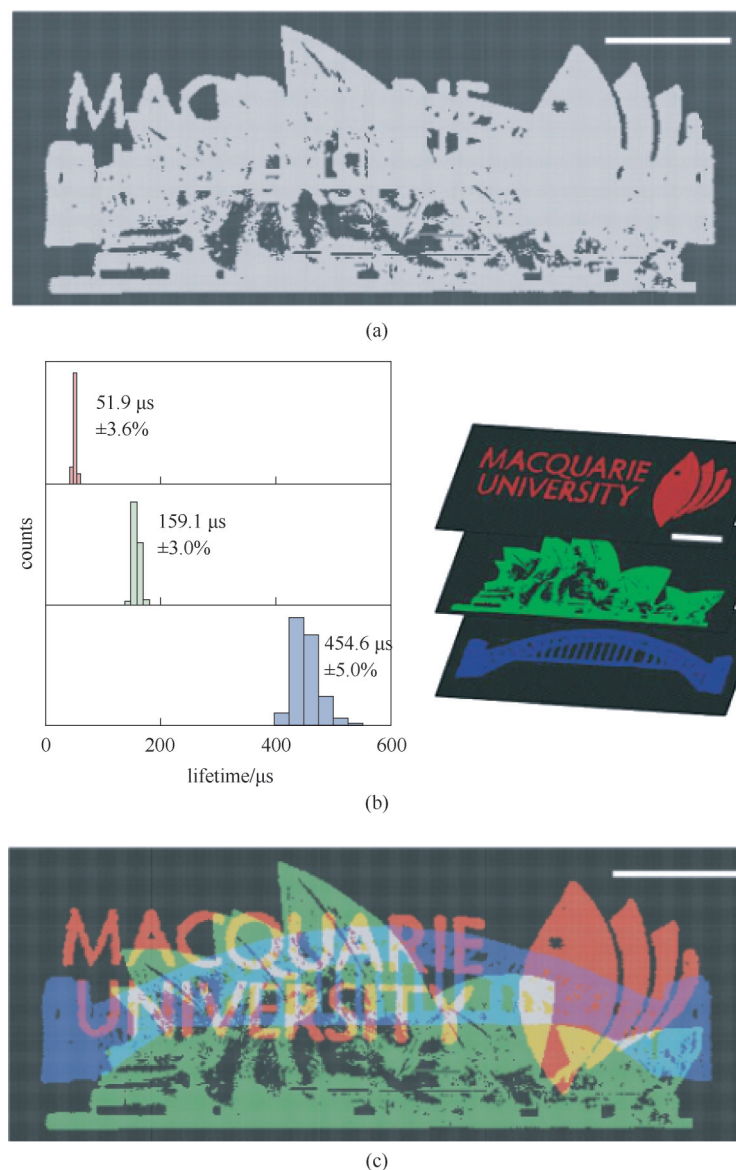


图 16 三个重叠的图案以不同的 Tm 掺杂纳米颗粒: ($C_{Yb} : C_{Tm}$) 20 : 4 为“麦考瑞大学”的标志, 20 : 1 为悉尼歌剧院的形象, 20 : 0.5 为悉尼海港大桥的形象。基于强度的发光成像只能给出一个复杂的图像(a), 根据每个像素的寿命份量时间分辨扫描分离图案(b), 解码包含在文档相同重叠空间中的真正的复用信息, 伪色用于表示每个像素的发光寿命(c)。所有图像比例尺均为 5 mm^[113]

Figure 16 Three overlapping patterns are printed with different Tm τ -dots : ($C_{Yb} : C_{Tm}$) 20 : 4 for the “Macquarie University” logo, 20 : 1 for the “Sydney Opera House” image, and 20 : 0.5 for the “Sydney Harbour Bridge” image. Intensity-based luminescence imaging only gives a complex picture (a), but time-resolved scanning separates the patterns based on the lifetime components of every pixel (b), so that genuine multiplexing information contained in the same overlapping space of the document can be decoded, pseudocolour is used to indicate the luminescence lifetime for each pixel(c). All images scale bars are 5 mm^[113]

力。特别是其独特的反斯托克斯位移发光特性, 为非侵入式的流体流速和温度测量等工程应用提供了新的可能性。因此, 进一步挖掘这类材料在工程实践中的价值至关重要。

但当前上转换发光材料仍面临一系列挑战。相较于荧光材料, 纳米级上转换材料的发光量子产率仍然较低, 提高其发光效率成为研究的重点。然而, 功能丰富的块状材料虽然有较高的发光效率, 但其的功能

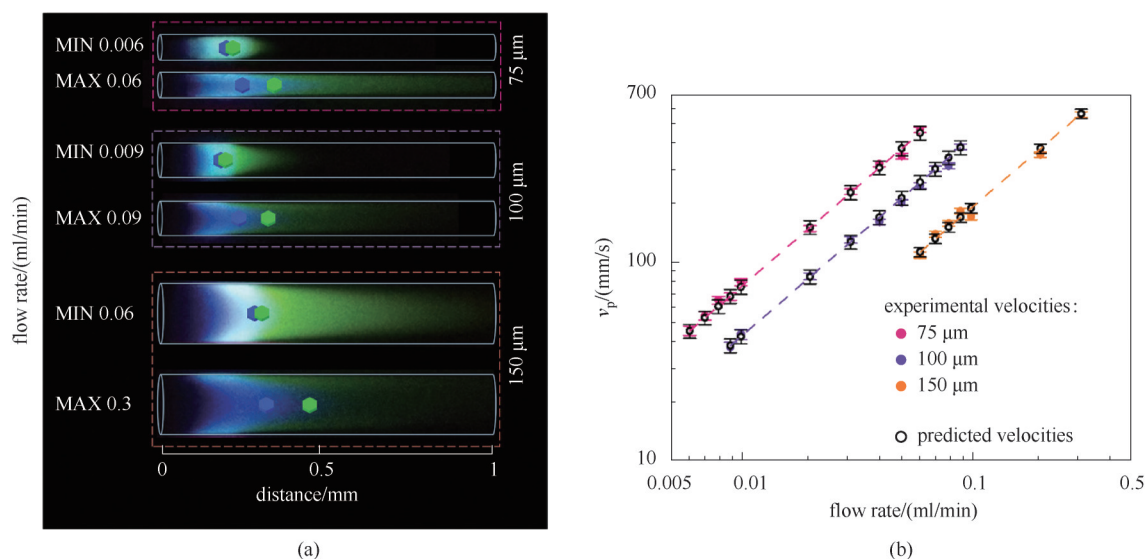


图17 使用直径为75、100和150 μm 毛细管并分别采用的最小和最大流量的多发射流线数字图像进行测量的示意图(蓝色和绿色六边形分别代表蓝色和绿色发射的最大值)(a); 多发射粒子测速的实验速度(彩色符号)和预测速度(黑色符号)图(b)^[125]

Figure 17 Schematic diagram of multi-emission streamline digital images measured using capillaries with diameters of 75, 100, and 150 μm , with both minimum and maximum flow rates (blue and green hexagons represent the maximum values of blue and green emissions) (a); Experimental velocity (color symbols) and predicted velocity (black symbols) of multi-emission particle velocity measurement (b)^[125]

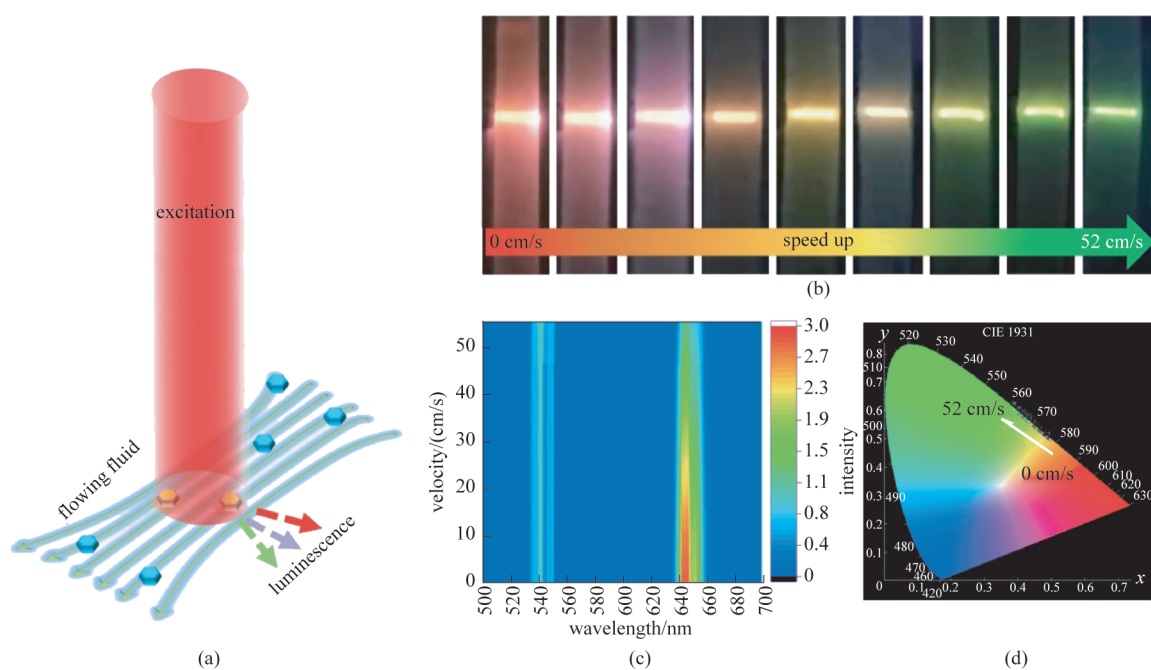


图18 上转换发光探测流体速度的机理示意图(a); 用980 nm激光激发不同流速下管内流体的照片(b); 6% Ce掺杂样品流动速率下捕获的上转换光谱(c); 色度图(CIE1931)上相应的发射颜色(d)^[126]

Figure 18 Schematic diagram of the upconversion luminescence mechanism sensitive to velocity (a); Photograph of the fluid inside the tube excited by a 980 nm laser at different flow rates (b); Upconversion spectrum captured at a flow rate of 6% Ce-doped sample (c); Corresponding emitted colors on the chromaticity diagram (CIE1931) (d)^[126]

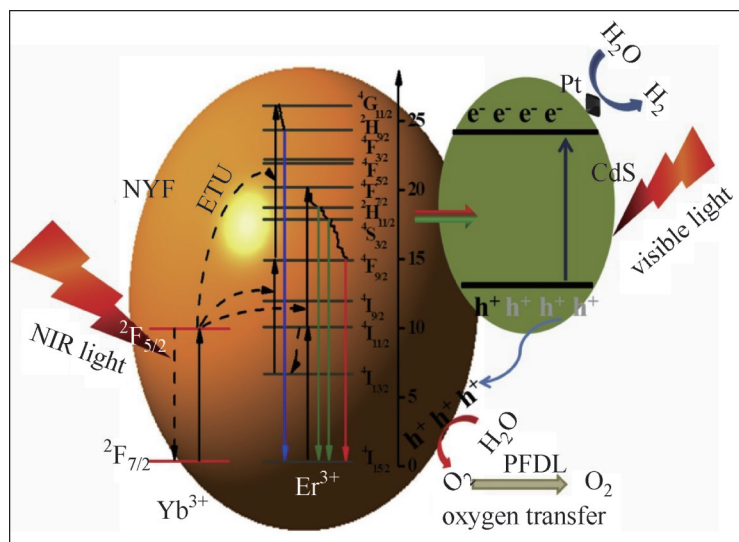


图19 近红外/可见光驱动Pt/CdS/NYF系统整体水分解示意图^[127]

Figure 19 Schematic of NIR/Visible-light-driven overall water split over Pt/CdS/NYF system^[127]

性差, 性用场景单一。特别是多层壳结构的上转换发光纳米颗粒的大规模合成, 仍是一个亟待解决的问题。另外, 在实际应用中, 上转换发光需要激光作为激发光源, 相较于传统荧光材料的可见光激发, 其光源的安全性和便携性仍需考虑。

尽管如此, 鉴于上转换材料的独特性质和稀土资

源的重要性, 克服这些挑战将带来巨大的收益。因此, 亟待更多科研人员投身于这一领域的研究, 共同推动稀土上转换材料在工程领域的更广泛应用。通过不断创新和努力, 有望解决上述问题, 为未来的工程实践和科技发展贡献更多力量。

参考文献

- [1] Auzel F. Upconversion and anti-Stokes processes with f and d ions in solids[J]. Chemical Reviews, 2004, 104(1): 139-173.
- [2] Bünzli J C G. Benefiting from the unique properties of lanthanide ions[J]. Accounts of Chemical Research, 2006, 39(1): 53-61.
- [3] 孙新雯. 稀土掺杂上转换发光NaLnF₄微米晶、纳米晶结构调控及其心血管疾病免疫检测应用[D]. 杭州: 浙江大学, 2020.
Sun X W. Structural evolution of rare earth doped NaLnF₄ micro/nanocrystal and application of immunoassay for cardiovascular diseases [D]. Hangzhou: Zhejiang University, 2020.
- [4] 唐宏武, 曹迪, 李诚予, 等. 低成本光镊装置在荧光定量检测中的应用[J]. 大学化学, 2015, 30(2): 50-55.
Tang H W, Cao D, Li C Y, et al. Application of a low-cost optical tweezers setup in fluorescence quantitative detection[J]. University Chemistry, 2015, 30(2): 50-55.
- [5] 刘冬梅, 陈秀梅, 袁泽, 等. 上转换纳米粒子的Y(OH)CO₃壳层包覆及壳层转化[J]. 物理化学学报, 2020, 36(7): 61-68.
Liu D M, Chen X M, Yuan Z, et al. Coating and transforming the Y(OH)CO₃ shell on upconversion nanoparticles[J]. Acta Physico-Chimica Sinica, 2020, 36(7): 61-68.
- [6] Dejneka M J, Streltsov A, Pal S, et al. Rare earth-doped glass microbarcodes[J]. Proceedings of the National Academy of Sciences of the United States of America, 2003, 100(2): 389-393.
- [7] Zijlmans H J M A A, Bonnet J, Burton J, et al. Detection of cell and tissue surface antigens using up-converting phosphors: a new reporter technology[J]. Analytical Biochemistry, 1999, 267(1): 30-36.
- [8] Auzel F. History of upconversion discovery and its evolution[J]. Journal of Luminescence, 2020, 223: 116900.
- [9] Sun Y P, Zhou B, Lin Y, et al. Quantum-sized carbon dots for bright and colorful photoluminescence[J]. Journal of the American Chemical

- Society, 2006, 128(24): 7756-7757.
- [10] Chen O, Shelby D E, Yang Y A, et al. Excitation-intensity-dependent color-tunable dual emissions from manganese-doped CdS/ZnS core/shell nanocrystals[J]. *Angewandte Chemie*, 2010, 122(52): 10330-10333.
- [11] Wu W Y, Li M J, Lian J E, et al. Efficient color-tunable multiexcitonic dual wavelength emission from type II semiconductor tetrapods[J]. *ACS Nano*, 2014, 8(9): 9349-9357.
- [12] Dong H, Sun L D, Yan C H. Basic understanding of the lanthanide related upconversion emissions[J]. *Nanoscale*, 2013, 5(13): 5703-5714.
- [13] Ai X Z, Ho C J H, Aw J, et al. *In vivo* covalent cross-linking of photon-converted rare-earth nanostructures for tumour localization and theranostics[J]. *Nature Communications*, 2016, 7: 10432.
- [14] Kumar P, Nagpal K, Gupta B K. Unclonable security codes designed from multicolor luminescent lanthanide-doped Y_2O_3 nanorods for anticounterfeiting[J]. *ACS Applied Materials & Interfaces*, 2017, 9(16): 14301-14308.
- [15] Bloembergen N. Solid state infrared quantum counters[J]. *Physical Review Letters*, 1959, 2(3): 84-85.
- [16] Liu Y J, Lu Y Q, Yang X S, et al. Amplified stimulated emission in upconversion nanoparticles for super-resolution nanoscopy[J]. *Nature*, 2017, 543(7644): 229-233.
- [17] Lee C, Xu E Z, Liu Y W, et al. Giant nonlinear optical responses from photon-avalanching nanoparticles[J]. *Nature*, 2021, 589(7841): 230-235.
- [18] Liang L L, Feng Z W, Zhang Q M, et al. Continuous-wave near-infrared stimulated-emission depletion microscopy using downshifting lanthanide nanoparticles[J]. *Nature Nanotechnology*, 2021, 16(9): 975-980.
- [19] Bednarkiewicz A, Chan E M, Kotulska A, et al. Photon avalanche in lanthanide doped nanoparticles for biomedical applications: super-resolution imaging[J]. *Nanoscale Horizons*, 2019, 4(4): 881-889.
- [20] Kolesov R, Lasse S, Rothfuchs C, et al. Superresolution microscopy of single rare-earth emitters in YAG and H3centers in diamond[J]. *Physical Review Letters*, 2018, 120(3): 033903.
- [21] Wen S H, Liu Y T, Wang F, et al. Nanorods with multidimensional optical information beyond the diffraction limit[J]. *Nature Communications*, 2020, 11: 6047.
- [22] Brites C D S, Balabhadra S, Carlos L D. Lanthanide-based thermometers: At the cutting-edge of luminescence thermometry[J]. *Advanced Optical Materials*, 2019, 7(5): 1801239.
- [23] Su X L, Wen Y, Yuan W, et al. Lifetime-based nanothermometry *in vivo* with ultra-long-lived luminescence[J]. *Chemical Communications*, 2020, 56(73): 10694-10697.
- [24] Goderski S, Runowski M, Woźny P, et al. Lanthanide upconverted luminescence for simultaneous contactless optical thermometry and manometry-sensing under extreme conditions of pressure and temperature[J]. *ACS Applied Materials & Interfaces*, 2020, 12(36): 40475-40485.
- [25] de Sousa Filho P C, Alain J, Leménager G, et al. Colloidal rare earth vanadate single crystalline particles as ratiometric luminescent thermometers[J]. *The Journal of Physical Chemistry C*, 2019, 123(4): 2441-2450.
- [26] Lacam A, Chateau C. High-pressure measurements at moderate temperatures in a diamond anvil cell with a new optical sensor: SrB_4O_7 : Sm^{2+} [J]. *Journal of Applied Physics*, 1989, 66(1): 366-372.
- [27] Xu C N, Watanabe T, Akiyama M, et al. Direct view of stress distribution in solid by mechanoluminescence[J]. *Applied Physics Letters*, 1999, 74(17): 2414-2416.
- [28] Chandra V K, Chandra B P, Jha P. Self-recovery of mechanoluminescence in $\text{ZnS}:\text{Cu}$ and $\text{ZnS}:\text{Mn}$ phosphors by trapping of drifting charge carriers[J]. *Applied Physics Letters*, 2013, 103(16): 161113.
- [29] Zhang H L, Peng D F, Wang W, et al. Mechanically induced light emission and infrared-laser-induced upconversion in the Er-doped CaZnOS multifunctional piezoelectric semiconductor for optical pressure and temperature sensing[J]. *The Journal of Physical Chemistry C*, 2015, 119(50): 28136-28142.
- [30] Xie L X, Qin Y, Chen H Y. Polymeric optodes based on upconverting nanorods for fluorescent measurements of pH and metal ions in blood samples[J]. *Analytical Chemistry*, 2012, 84(4): 1969-1974.
- [31] Näreoja T, Deguchi T, Christ S, et al. Ratiometric sensing and imaging of intracellular pH using polyethylenimine-coated photon upconversion nanoprobe[J]. *Analytical Chemistry*, 2017, 89(3): 1501-1508.
- [32] Ding C P, Cheng S S, Zhang C L, et al. Ratiometric upconversion luminescence nanoprobe with near-infrared Ag_2S nanodots as the energy

- acceptor for sensing and imaging of pH *in vivo*[J]. Analytical Chemistry, 2019, 91(11): 7181-7188.
- [33] Wang S, Feng J, Song S Y, et al. A long-wave optical pH sensor based on red upconversion luminescence of NaGdF₄ nanotubes[J]. RSC Advances, 2014, 4(99): 55897-55899.
- [34] Li Z H, Yuan H, Yuan W, et al. Upconversion nanoprobe for biodetections[J]. Coordination Chemistry Reviews, 2018, 354: 155-168.
- [35] Bigdeli A, Ghasemi F, Abbasi-Moayed S, et al. Ratiometric fluorescent nanoprobe for visual detection: design principles and recent advances - A review[J]. Analytica Chimica Acta, 2019, 1079: 30-58.
- [36] Deng R R, Qin F, Chen R F, et al. Temporal full-colour tuning through non-steady-state upconversion[J]. Nature Nanotechnology, 2015, 10(3): 237-242.
- [37] Park B J, Hong A R, Park S, et al. Flexible transparent displays based on core/shell upconversion nanophosphor-incorporated polymer waveguides[J]. Scientific Reports, 2017, 7: 45659.
- [38] Gao L X, Shan X C, Xu X X, et al. Video-rate upconversion display from optimized lanthanide ion doped upconversion nanoparticles[J]. Nanoscale, 2020, 12(36): 18595-18599.
- [39] Jia H, Li D G, Zhang D, et al. High color-purity red, green, and blue-emissive core-shell upconversion nanoparticles using ternary near-infrared quadrature excitations[J]. ACS Applied Materials & Interfaces, 2021, 13(3): 4402-4409.
- [40] RokMK, JihoonK, YeonLJ, et al. Elemental-migration-assisted full-color-tunable upconversion nanoparticles for video-rate three-dimensional volumetric displays[J]. Nano Letters, 2023, 23(7): 3014-3022.
- [41] Hong A R, Kyhm J H, Kang G M, et al. Orthogonal R/G/B upconversion luminescence-based full-color tunable upconversion nanophosphors for transparent displays[J]. Nano Letters, 2021, 21(11): 4838-4844.
- [42] Huang K F, Qiu H Y, Zhang X T, et al. Orthogonal trichromatic upconversion with high color purity in core-shell nanoparticles for a full-color display[J]. Angewandte Chemie (International Ed in English), 2023, 62(14): e202218491.
- [43] Dong H, Sun L D, Yan C H. Energy transfer in lanthanide upconversion studies for extended optical applications[J]. Chemical Society Reviews, 2015, 44(6): 1608-1634.
- [44] Renero-Lecuna C, Martín-Rodríguez R, Valiente R, et al. Origin of the high upconversion green luminescence efficiency in β -NaYF₄: 2%Er³⁺, 20%Yb³⁺[J]. Chemistry of Materials, 2011, 23(15): 3442-3448.
- [45] Chen G Y, Ohulchanskyy T Y, Kumar R, et al. Ultrasmall monodisperse NaYF₄:Yb³⁺/Tm³⁺ nanocrystals with enhanced near-infrared to near-infrared upconversion photoluminescence[J]. ACS Nano, 2010, 4(6): 3163-3168.
- [46] Mai H X, Zhang Y W, Sun L D, et al. Highly efficient multicolor up-conversion emissions and their mechanisms of monodisperse NaYF₄: Yb, Er core and core/shell-structured nanocrystals[J]. The Journal of Physical Chemistry C, 2007, 111(37): 13721-13729.
- [47] Boyer J C, Vetrone F, Cuccia L A, et al. Synthesis of colloidal upconverting NaYF₄ nanocrystals doped with Er³⁺, Yb³⁺ and Tm³⁺, Yb³⁺ via thermal decomposition of lanthanide trifluoroacetate precursors[J]. Journal of the American Chemical Society, 2006, 128(23): 7444-7445.
- [48] Wang G F, Peng Q, Li Y D. Upconversion luminescence of monodisperse CaF₂:Yb³⁺/Er³⁺ nanocrystals[J]. Journal of the American Chemical Society, 2009, 131(40): 14200-14201.
- [49] Chen G Y, Yang C H, Prasad P N. Nanophotonics and nanochemistry: controlling the excitation dynamics for frequency up- and down-conversion in lanthanide-doped nanoparticles[J]. Accounts of Chemical Research, 2013, 46(7): 1474-1486.
- [50] Feng W, Han C M, Li F Y. Upconversion-nanophosphor-based functional nanocomposites[J]. Advanced Materials, 2013, 25(37): 5287-5303.
- [51] Liang Y S, Zhu Z M, Qiao S Q, et al. Migrating photon avalanche in different emitters at the nanoscale enables 46th-order optical nonlinearity[J]. Nature Nanotechnology, 2022, 17(5): 524-530.
- [52] Chivian J S, Case W E, Eden D D. The photon avalanche: a new phenomenon in Pr³⁺-based infrared quantum counters[J]. Applied Physics Letters, 1979, 35(2): 124-125.
- [53] Collings B C, Silversmith A J. Avalanche upconversion in LaF₃:Tm³⁺[J]. Journal of Luminescence, 1994, 62(6): 271-279.
- [54] Muñoz T, Balkus K J. Preparation of oriented zeolite UTD-1 membranes via pulsed laser ablation[J]. Journal of the American Chemical Society, 1999, 121(1): 139-146.
- [55] Wang F, Deng R R, Wang J, et al. Tuning upconversion through energy migration in core-shell nanoparticles[J]. Nature Materials, 2011, 10(12): 968-973.
- [56] Zhou B, Yang W F, Han S Y, et al. Photon upconversion through Tb³⁺-mediated interfacial energy transfer[J]. Advanced Materials, 2015, 27(40): 6208-6212.

- [57] Zhou J F, Wu Z S, Zhang Z J, et al. Study on an antiwear and extreme pressure additive of surface coated LaF_3 nanoparticles in liquid paraffin[J]. *Wear*, 2001, 249(5-6): 333-337.
- [58] Stouwdam J W, van Veggel F C J M. Near-infrared emission of redispersible Er^{3+} , Nd^{3+} , and Ho^{3+} doped LaF_3 nanoparticles[J]. *Nano Letters*, 2002, 2(7): 733-737.
- [59] Li Z Q, Zhang Y. Monodisperse silica-coated polyvinylpyrrolidone/ NaYF_4 nanocrystals with multicolor upconversion fluorescence emission[J]. *Angewandte Chemie*, 2006, 118(46): 7896-7899.
- [60] Ptacek P, Schäfer H, Kömpe K, et al. Crystal phase control of luminescing $\alpha\text{-NaGdF}_4\text{:Eu}^{3+}$ and $\beta\text{-NaGdF}_4\text{:Eu}^{3+}$ nanocrystals[J]. *Advanced Functional Materials*, 2007, 17(18): 3843-3848.
- [61] Qian H S, Zhang Y. Synthesis of hexagonal-phase core-shell NaYF_4 nanocrystals with tunable upconversion fluorescence[J]. *Langmuir*, 2008, 24(21): 12123-12125.
- [62] Heer S, Kömpe K, Güdel H U, et al. Highly efficient multicolour upconversion emission in transparent colloids of lanthanide-doped NaYF_4 nanocrystals[J]. *Advanced Materials*, 2004, 16(23/24): 2102-2105.
- [63] Zeng J H, Su J, Li Z H, et al. Synthesis and upconversion luminescence of hexagonal-phase $\text{NaYF}_4\text{:Yb, Er}^{3+}$ phosphors of controlled size and morphology[J]. *Advanced Materials*, 2005, 17(17): 2119-2123.
- [64] Wang X, Zhuang J, Peng Q, et al. A general strategy for nanocrystal synthesis[J]. *Nature*, 2005, 437(7055): 121-124.
- [65] Kobayashi S, Hiroishi K, Tokunoh M, et al. Chelating properties of linear and branched poly(ethylenimines)[J]. *Macromolecules*, 1987, 20(7): 1496-1500.
- [66] Zhang Y W, Sun X, Si R, et al. Single-crystalline and monodisperse LaF_3 triangular nanoplates from a single-source precursor[J]. *Journal of the American Chemical Society*, 2005, 127(10): 3260-3261.
- [67] Mai H X, Zhang Y W, Si R, et al. High-quality sodium rare-earth fluoride nanocrystals: controlled synthesis and optical properties[J]. *Journal of the American Chemical Society*, 2006, 128(19): 6426-6436.
- [68] Boyer J C, Cuccia L A, Capobianco J A. Synthesis of colloidal upconverting $\text{NaYF}_4\text{:Er}^{3+}/\text{Yb}^{3+}$ and $\text{Tm}^{3+}/\text{Yb}^{3+}$ monodisperse nanocrystals[J]. *Nano Letters*, 2007, 7(3): 847-852.
- [69] Yi G, Chow G. Synthesis of hexagonal-phase $\text{NaYF}_4\text{:Yb, Er}$ and $\text{NaYF}_4\text{:Yb, Tm}$ nanocrystals with efficient up-conversion fluorescence[J]. *Advanced Functional Materials*, 2006, 16(18): 2324-2329.
- [70] Wei Y, Lu F Q, Zhang X R, et al. Synthesis of oil-dispersible hexagonal-phase and hexagonal-shaped $\text{NaYF}_4\text{:Yb, Er}$ nanoplates[J]. *Chemistry of Materials*, 2006, 18(24): 5733-5737.
- [71] Yi G S, Chow G M. Water-soluble $\text{NaYF}_4\text{:Yb, Er(Tm)/NaYF}_4$ /polymer core/shell/shell nanoparticles with significant enhancement of upconversion fluorescence[J]. *Chemistry of Materials*, 2007, 19(3): 341-343.
- [72] Gnanasammandhan M K, Idris N M, Bansal A, et al. Near-IR photoactivation using mesoporous silica-coated $\text{NaYF}_4\text{:Yb, Er/Tm}$ upconversion nanoparticles[J]. *Nature Protocols*, 2016, 11(4): 688-713.
- [73] Wang F, Deng R R, Liu X G. Preparation of core-shell NaGdF_4 nanoparticles doped with luminescent lanthanide ions to be used as upconversion-based probes[J]. *Nature Protocols*, 2014, 9(7): 1634-1644.
- [74] Li X M, Shen D K, Yang J P, et al. Successive layer-by-layer strategy for multi-shell epitaxial growth: shell thickness and doping position dependence in upconverting optical properties[J]. *Chemistry of Materials*, 2013, 25(1): 106-112.
- [75] Johnson N J J, Korinek A, Dong C H, et al. Self-focusing by Ostwald ripening: a strategy for layer-by-layer epitaxial growth on upconverting nanocrystals[J]. *Journal of the American Chemical Society*, 2012, 134(27): 11068-11071.
- [76] Fadeel B, Garcia-Bennett A E. Better safe than sorry: understanding the toxicological properties of inorganic nanoparticles manufactured for biomedical applications[J]. *Advanced Drug Delivery Reviews*, 2010, 62(3): 362-374.
- [77] Choi H S, Liu W H, Misra P, et al. Renal clearance of quantum dots[J]. *Nature Biotechnology*, 2007, 25(10): 1165-1170.
- [78] Kawagoe M, Hirasawa F, Wang S C, et al. Orally administrated rare earth element cerium induces metallothionein synthesis and increases glutathione in the mouse liver[J]. *Life Sciences*, 2005, 77(8): 922-937.
- [79] Hardman R. A toxicologic review of quantum dots: toxicity depends on physicochemical and environmental factors[J]. *Environmental Health Perspectives*, 2006, 114(2): 165-172.
- [80] Kawagoe M, Ishikawa K, Wang S C, et al. Acute effects on the lung and the liver of oral administration of cerium chloride on adult, neonatal and fetal mice[J]. *Journal of Trace Elements in Medicine and Biology*, 2008, 22(1): 59-65.

- [81] Krug H F, Wick P. Nanotoxicology: an interdisciplinary challenge[J]. *Angewandte Chemie (International Ed in English)*, 2011, 50(6): 1260-1278.
- [82] Kunzmann A, Andersson B, Thurnherr T, et al. Toxicology of engineered nanomaterials: focus on biocompatibility, biodistribution and biodegradation[J]. *Biochimica et Biophysica Acta (BBA) - General Subjects*, 2011, 1810(3): 361-373.
- [83] Wang F, Liu X G. Multicolor tuning of lanthanide-doped nanoparticles by single wavelength excitation[J]. *Accounts of Chemical Research*, 2014, 47(4): 1378-1385.
- [84] Dong H, Du S R, Zheng X Y, et al. Lanthanide nanoparticles: from design toward bioimaging and therapy[J]. *Chemical Reviews*, 2015, 115(19): 10725-10815.
- [85] Zheng W, Huang P, Tu D T, et al. Lanthanide-doped upconversion nano-bioprobes: electronic structures, optical properties, and biodetection [J]. *Chemical Society Reviews*, 2015, 44(6): 1379-1415.
- [86] Wang Y, Zheng K Z, Song S Y, et al. Remote manipulation of upconversion luminescence[J]. *Chemical Society Reviews*, 2018, 47(17): 6473-6485.
- [87] Zhao J B, Jin D Y, Schartner E P, et al. Single-nanocrystal sensitivity achieved by enhanced upconversion luminescence[J]. *Nature Nanotechnology*, 2013, 8(10): 729-734.
- [88] Kumar B, Malhotra K, Fuku R, et al. Recent trends in the developments of analytical probes based on lanthanide-doped upconversion nanoparticles[J]. *TrAC Trends in Analytical Chemistry*, 2021, 139: 116256.
- [89] Gnach A, Lipinski T, Bednarkiewicz A, et al. Upconverting nanoparticles: assessing the toxicity[J]. *Chemical Society Reviews*, 2015, 44(6): 1561-1584.
- [90] Wang J A, Wang F, Wang C, et al. Single-band upconversion emission in lanthanide-doped KMnF_3 nanocrystals[J]. *Angewandte Chemie International Edition*, 2011, 50(44): 10369-10372.
- [91] Tian G, Gu Z J, Zhou L J, et al. Mn^{2+} dopant-controlled synthesis of $\text{NaYF}_4:\text{Yb}/\text{Er}$ upconversion nanoparticles for *in vivo* imaging and drug delivery[J]. *Advanced Materials*, 2012, 24(9): 1226-1231.
- [92] Zhao M Y, Sik A, Zhang H X, et al. Tailored NIR- II lanthanide luminescent nanocrystals for improved biomedical application[J]. *Advanced Optical Materials*, 2023, 11(11):2202039.
- [93] Zhong Y T, Ma Z R, Zhu S J, et al. Boosting the down-shifting luminescence of rare-earth nanocrystals for biological imaging beyond 1500 nm[J]. *Nature Communications*, 2017, 8: 737.
- [94] Zhong Y T, Dai H J. A mini-review on rare-earth down-conversion nanoparticles for NIR- II imaging of biological systems[J]. *Nano Research*, 2020, 13(5): 1281-1294.
- [95] Yang Y W, Chen Y, Pei P, et al. Fluorescence-amplified nanocrystals in the second near-infrared window for *in vivo* real-time dynamic multiplexed imaging[J]. *Nature Nanotechnology*, 2023, 18(10): 1195-1204.
- [96] Agostinis P, Berg K, Cengel K A, et al. Photodynamic therapy of cancer: an update[J]. *CA: A Cancer Journal for Clinicians*, 2011, 61(4): 250-281.
- [97] Lucky S S, Soo K C, Zhang Y. Nanoparticles in photodynamic therapy[J]. *Chemical Reviews*, 2015, 115(4): 1990-2042.
- [98] Shanmugam V, Selvakumar S, Yeh C S. Near-infrared light-responsive nanomaterials in cancer therapeutics[J]. *Chemical Society Reviews*, 2014, 43(17): 6254-6287.
- [99] Liu Y Y, Meng X F, Bu W B. Upconversion-based photodynamic cancer therapy[J]. *Coordination Chemistry Reviews*, 2019, 379: 82-98.
- [100] Fan W P, Tang W, Lau J, et al. Breaking the depth dependence by nanotechnology-enhanced X-ray-excited deep cancer theranostics[J]. *Advanced Materials*, 2019, 31(12): 1806381.
- [101] Zhao H X, Li Y T, Zhang X B, et al. Orthogonal excitations of lanthanide nanoparticle up/down conversion emissions via switching NIR lights for *in-vivo* theranostics[J]. *Biomaterials*, 2022, 291: 121873.
- [102] Meruga J M, Baride A, Cross W, et al. Red-green-blue printing using luminescence-upconversion inks[J]. *Journal of Materials Chemistry C*, 2014, 2(12): 2221-2227.
- [103] Wang C L, Jin Y H, Yuan L F, et al. A spatial/temporal dual-mode optical thermometry platform based on synergetic luminescence of Ti^{4+} - Eu^{3+} embedded flexible 3D micro-rod arrays: high-sensitive temperature sensing and multi-dimensional high-level secure anti-counterfeiting [J]. *Chemical Engineering Journal*, 2019, 374: 992-1004.
- [104] Wu T Q, Boyer J C, Barker M, et al. A "plug-and-play" method to prepare water-soluble photoresponsive encapsulated upconverting

- nanoparticles containing hydrophobic molecular switches[J]. *Chemistry of Materials*, 2013, 25(12): 2495-2502.
- [105] Ding M Y, Chen D Q, Ma D Y, et al. Tuning the upconversion luminescence lifetimes of $\text{KYb}_2\text{F}_7\text{:Ho}^{3+}$ nanocrystals for optical multiplexing[J]. *ChemPhysChem*, 2015, 16(18): 3784-3789.
- [106] Liu X, Chen Z H, Zhang H X, et al. Independent luminescent lifetime and intensity tuning of upconversion nanoparticles by gradient doping for multiplexed encoding[J]. *Angewandte Chemie (International Ed in English)*, 2021, 60(13): 7041-7045.
- [107] Liu H L, Xu J H, Wang H, et al. Secure printing: tunable resonator-upconverted emission (TRUE) color printing and applications in optical security[J]. *Advanced Materials*, 2019, 31(15): 1807900.
- [108] Li M X, Yao W J, Liu J, et al. Facile synthesis and screen printing of dual-mode luminescent $\text{NaYF}_4\text{:Er, Yb (Tm)/carbon dots}$ for anti-counterfeiting applications[J]. *Journal of Materials Chemistry C*, 2017, 5(26): 6512-6520.
- [109] Han Y D, Gao C, Wang Y B, et al. Spatially confined luminescence process in tip-modified heterogeneous-structured microrods for high-level anti-counterfeiting[J]. *Physical Chemistry Chemical Physics*, 2018, 20(14): 9516-9522.
- [110] Sandhyarani A, Kokila M K, Darshan G P, et al. Versatile core-shell $\text{SiO}_2\text{@SrTiO}_3\text{:Eu}^{3+}, \text{Li}^+$ nanopowders as fluorescent label for the visualization of latent fingerprints and anti-counterfeiting applications[J]. *Chemical Engineering Journal*, 2017, 327: 1135-1150.
- [111] Li Y Y, You W W, Zhao J, et al. Unique excitation power density and pulse width-dependent multicolor upconversion emissions of $\text{Y}_2\text{Mo}_4\text{O}_{15}\text{:Yb}^{3+}, \text{Ho}^{3+}$ for anti-counterfeiting and information encryption applications[J]. *Journal of Materials Chemistry C*, 2023, 11(2): 546-553.
- [112] Gao D L, Gao J, Gao F, et al. Quintuple-mode dynamic anti-counterfeiting using multi-mode persistent phosphors[J]. *Journal of Materials Chemistry C*, 2021, 9(46): 16634-16644.
- [113] Lu Y Q, Zhao J B, Zhang R, et al. Tunable lifetime multiplexing using luminescent nanocrystals[J]. *Nature Photonics*, 2014, 8(1): 32-36.
- [114] Li X M, Guo Z Z, Zhao T C, et al. Filtration shell mediated power density independent orthogonal excitations – emissions upconversion luminescence[J]. *Angewandte Chemie International Edition*, 2016, 55(7): 2464-2469.
- [115] Ma Q Q, Wang J, Li Z H, et al. Near-infrared-light-mediated high-throughput information encryption based on the inkjet printing of upconversion nanoparticles[J]. *Inorganic Chemistry Frontiers*, 2017, 4(7): 1166-1172.
- [116] Dong H, Sun L D, Feng W, et al. Versatile spectral and lifetime multiplexing nanoplatfrom with excitation orthogonalized upconversion luminescence[J]. *ACS Nano*, 2017, 11(3): 3289-3297.
- [117] Sun T Y, Xu B Z, Chen B, et al. Anti-counterfeiting patterns encrypted with multi-mode luminescent nanotagants[J]. *Nanoscale*, 2017, 9(8): 2701-2705.
- [118] Zuo J, Li Q Q, Xue B, et al. Employing shells to eliminate concentration quenching in photonic upconversion nanostructure[J]. *Nanoscale*, 2017, 9(23): 7941-7946.
- [119] Rodrigues E M, Gállico D A, Lemes M A, et al. One pot synthesis and systematic study of the photophysical and magnetic properties and thermal sensing of α and β -phase NaLnF_4 and β -phase core@shell nanoparticles[J]. *New Journal of Chemistry*, 2018, 42(16): 13393-13405.
- [120] Dong N N, Pedroni M, Piccinelli F, et al. NIR-to-NIR two-photon excited $\text{CaF}_2\text{:Tm}^{3+}, \text{Yb}^{3+}$ nanoparticles: multifunctional nanoprobe for highly penetrating fluorescence bio-imaging[J]. *ACS Nano*, 2011, 5(11): 8665-8671.
- [121] Wang X F, Zheng J, Xuan Y, et al. Optical temperature sensing of $\text{NaYbF}_4\text{:Tm}^{3+}\text{@SiO}_2$ core-shell micro-particles induced by infrared excitation[J]. *Optics Express*, 2013, 21(18): 21596.
- [122] Xu M, Chen D Q, Huang P, et al. A dual-functional upconversion core@shell nanostructure for white-light-emission and temperature sensing[J]. *Journal of Materials Chemistry C*, 2016, 4(27): 6516-6524.
- [123] Ishiwada N, Fujioka S, Ueda T, et al. Co-doped $\text{Y}_2\text{O}_3\text{:Tb}^{3+}/\text{Tm}^{3+}$ multicolor emitting phosphors for thermometry[J]. *Optics Letters*, 2011, 36(5): 760-762.
- [124] Zou Q, Marcelot C, Ratel-Ramond N, et al. Heterogeneous oxysulfide@fluoride core/shell nanocrystals for upconversion-based nanothermometry[J]. *ACS nano*, 2022, 16(8): 12107-12117.
- [125] Tessitore G, Maurizio S L, Sabri T, et al. Multiemission particle velocimetry: the key role of intrinsic lifetime dynamics from upconverting nanosystems in multiemission particle velocimetry[J]. *Advanced Materials*, 2020, 32(42):2002266.
- [126] Huang H, Wang S X, Chen R Y, et al. Engineering upconverting core-shell nano-probe for spectral responsive fluid velocimetry[J]. *Nano Research*, 2023, 16(1): 1212-1219.
- [127] Gao W, Tian B, Zhang W Y, et al. NIR light driven catalytic hydrogen generation over semiconductor photocatalyst coupling up-conversion

- component[J]. *Applied Catalysis B: Environmental*, 2019, 257: 117908.
- [128] Ansari A A, Sillanpää M. Advancement in upconversion nanoparticles based NIR-driven photocatalysts[J]. *Renewable and Sustainable Energy Reviews*, 2021, 151: 111631.
- [129] Tian Q Y, Yao W J, Wu W, et al. NIR light-activated upconversion semiconductor photocatalysts[J]. *Nanoscale Horizons*, 2019, 4(1): 10-25.
- [130] Zhang Q Z, Yang F, Xu Z H, et al. Are lanthanide-doped upconversion materials good candidates for photocatalysis? [J]. *Nanoscale Horizons*, 2019, 4(3): 579-591.
- [131] Acosta-Mora P, Domen K, Hisatomi T, et al. Shifting the NIR into the UV-blue: up-conversion boosted photocatalysis[J]. *Optical Materials*, 2018, 83: 315-320.
- [132] Zhang Y Y, Lan X F, Park S H, et al. Rational design of efficient near-infrared photon conversion channel via dual-upconversion process for superior photocatalyst[J]. *Carbon*, 2020, 169: 111-117.

Research Progress of Rare Earth Doped Upconversion Luminescent Materials

Jia Song, Wang Xuefei*, Shi Yishi

School of Chemistry Engineering, University of Chinese Academy of Sciences, Beijing 101408, China

Abstract: Upconversion luminescence is a kind of anti-stokes shift luminescence. The upconversion luminescent materials which usually composed by rear earth elements and have some properties superior to ordinary organic materials, such as long luminous lifetime, photobleaching resistance, narrow emission bands and so on. Therefore, this unique phenomenon that absorbing low energy photons and emitting high energy photons has been attracted the attention of researchers in many fields. In this review, the most common mechanism of energy transfer upconversion was described in detail, two types of complexed lanthanide ions-mediated energy migration upconversion mechanism that realized though core-shell structure and other upconversion mechanisms were also introduced. The synthesis methods that most widely reported Co-precipitation method in recently for preparing core or core multi-shells upconversion nanoparticles and hydrothermal method that widely used for preparation bulk materials were introduced. Importantly, due to the abundant emission bands of these lanthanide doped nanoparticles and the strongly penetration of near-infrared laser, these nanoparticles have been used in biological domain, such as photodynamic therapy to eliminate tumors or some bacteria, cell and tissue imaging that achieved sub-centimeter depth. In addition, colorful upconversion luminescent materials with the feature of multi-mode color tuning were used in high-level anti-counterfeiting, optical information storage and transparent display. Furthermore, the upconversion nanoparticles are expected to be applied to the engineering projects based on the changes of emission characters that originated from the influence of the temperature or fluid rate to the population of lanthanide ions and this non-invasive optical method requires simple equipment with low cost that could obtain accurate results. Besides, the upconversion materials that excited by near-infrared light seems like more promising to use the solar energy, more photocatalysts base on the upconversion materials that used the near-infrared light as the excitation resource rather than visible or ultraviolet light. So far, more and more nano-scale upconversion materials have been reported and used instead of bulk materials, because of their extraordinary modification potential though the construction of core-shell projects. However, the biggest obstacle limiting the applications of upconversion luminescent materials remains the extremely low quantum yield. In addition to the reason of the upconversion mechanism itself, the absorption cross-section of the lanthanide elements is too small and cannot be compared with organic dyes. The problem of low luminous efficiency needs to be solved urgently. On the premise of ensuring functionality, the structure of upconversion nanoparticles should also be simplified to reduce the difficulty of synthesis and elevate synthesis yield, and some new generation mechanisms for upconversion luminescence modulation needs to be found that requires the joint efforts of more relevant researchers to expanding the applications of upconversion luminescent materials.

Keywords: rare earth elements; upconversion nanoparticles; luminescent materials; doping