

激光与光电子学进展

二维材料体系激子上转换发光研究进展(特邀)

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摘要 上转换发光即发射光子能量高于激发光子能量的反斯托克斯过程,可以有效实现能量重整与转化,在生物成像、太阳能电池、光催化及光制冷等方面有着巨大应用前景。作为后摩尔时代战略性新材料,二维材料由于激子偶极矩强度大、线宽窄、无序性低、束缚能高等优势,为实现室温高效激子上转换发光创造了有利条件,近年来吸引了研究者的广泛兴趣。本文首先介绍实现光子上转换的发光机制,包括声子辅助、双光子吸收、俄歇复合等途径,进而梳理基于六方氮化硼、单层过渡金属二硫化物、二维钙钛矿等典型二维材料体系的上转换发光效应研究,同时针对上转换发光效率低的问题,讨论对二维材料上转换发光的调控和增强方式,最后展望二维材料体系激子上转换发光效应的应用前景。

关键词 上转换发光; 材料; 二维材料; 激子; 非线性光学

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Research Progress on Excitonic Upconversion Photoluminescence in Two-Dimensional Materials (Invited)

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Abstract Upconversion photoluminescence, an anti-Stokes process in which the emitted photon energy exceeds the excitation photon energy, can effectively achieve energy renormalization and conversion, with great application prospects in fields such as biological imaging, solar cells, photocatalysis, and optical refrigeration. As a strategically important new material in the post-Moore era, two-dimensional materials are crucial in realizing efficient room-temperature excitonic upconversion because of their large dipole moments, narrow linewidths, low disorder, and high exciton binding energies, which have recently attracted extensive research interest. This study first introduces the luminescence mechanisms used to achieve photon upconversion, including phonon-assisted upconversion, two-photon absorption, and Auger recombination. Then, research on upconversion based on two-dimensional material systems, such as hexagonal boron nitride, monolayer transition metal dichalcogenides, and two-dimensional perovskites, is summarized. Modulation and enhancement approaches for upconversion in two-dimensional materials that target low upconversion efficiency are also discussed. Finally, application prospects of excitonic upconversion effects in two-dimensional material systems are envisioned.

Key words upconversion photoluminescence; materials; two-dimensional materials; excitons; nonlinear optics

1 引言

光学频率上转换过程是将一个或几个低能量光子转换成高能量光子,从而使出射光的频率高于入射光的反斯托克斯过程,可以有效实现能量重整与转化,在生物成像、太阳能电池、光催化及光制冷等方面有着巨大应用前景。目前,实现光学频率上转换的物理机制

主要包括声子辅助上转换、多光子上转换、俄歇复合上转换等。1929年,Pringsheim^[1]便提出声子辅助上转换概念:在单色光辐照下,样品可同时吸收光子和声子,辐射出光子能量高于入射光的荧光,带走材料体系中的声子进而降低温度。此后声子辅助上转换被广泛应用于生物成像^[2]、红外探测^[3]、光学制冷^[4-5]和光伏^[6]等领域。1931年,Göppert-Mayer^[7]通过理论预测物质在

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强光激发下可同时吸收两个光子跃迁至高能态,产生双光子荧光效应,由此开辟了光学频率上转换又一支。以此为基础的双光子显微镜成为了显微领域的突破性技术^[8],在激光光源^[9]和三维荧光显微^[10]等技术领域的应用也引起了研究者的极大兴趣。1963年,Parker和Hatchard^[11-12]首次报道了基于三重态-三重态湮灭的上转换发光体系,从而引入通过俄歇复合实现上转换发光的新机制。在这种机制中,两个激发态电子之间发生能量转移,一个电子回到基态,另一个电子被激发到更高能级并通过辐射跃迁回到基态而发光,即发生了上转换发光现象。此类上转换发光机制由于效率高且不需要相干光源,在提高太阳能电池效率^[13-15]和荧光生物显微成像^[16-18]方面具备潜在应用价值。

二维材料由于具有激子偶极矩强度大、线宽窄、无序性低、束缚能高等优势,有望实现室温高效激子上转换发光,为探索光学频率上转换发光提供了一个全新平台。作为后摩尔时代战略性新材料,二维材料自从2004年被发现以来^[19],其原子级厚度、良好的结构稳定性和强非线性光学响应等优良的物理光电特性便被广泛关注^[20-23]。相比体材料,二维材料的介电屏蔽作

用较弱,因此载流子之间的库仑相互作用显著增强,从而形成了丰富的稳定多载流子复合物,如激子、带电激子、双激子等。研究表明,利用载流子与载流子、载流子与声子之间的耦合,在二维材料中也可以实现光学频率上转换发光。尤其是激子等准粒子的存在,为二维材料上转换发光引入了基于带电激子-激子共振的声子辅助上转换和基于激子效应的俄歇复合上转换等新颖物理机制。而层数对二维材料物理性质的显著影响也为上转换发光的调控提供了新自由度,并由此诞生了转角堆叠、异质结堆叠等独特调控方法。最近研究表明二维材料中激子上转换发光在温度传感^[24]、生物示踪治疗^[25]、微纳尺度的光学制冷^[26]等领域有广泛应用前景,但更深入的物理机制分析和更高性能器件构筑还有待进一步探索。

本文聚焦近年来二维材料体系激子上转换发光研究,如图1所示。首先介绍上转换发光机制包括声子辅助、双光子吸收、俄歇复合等,探讨二维材料上转换发光的主要物理机制和基本原理;其次梳理基于六方氮化硼、单层过渡金属二硫化物、二维钙钛矿等典型二维材料体系中上转换发光效应研究;随后针对上转换发光效率低的问题,讨论对二维材料上转换发光的调

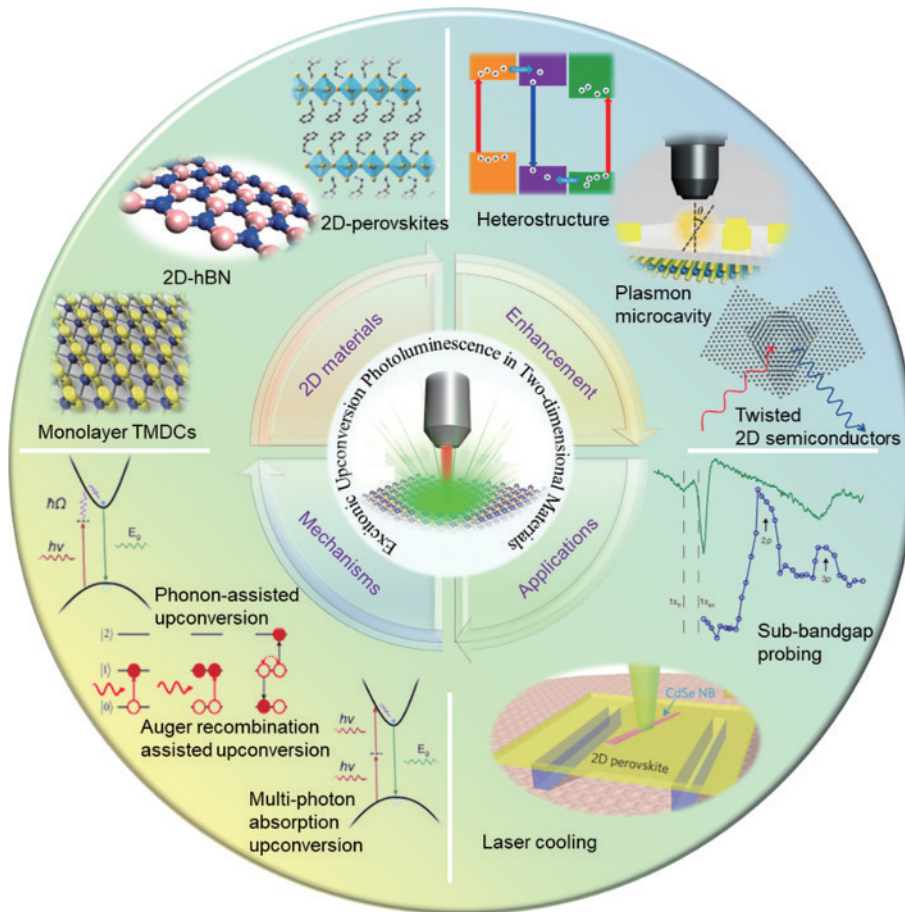


图1 二维材料激子上转换发光机制、材料体系、增强方式及应用

Fig. 1 Mechanisms, materials systems, enhancement approaches, and applications of excitonic upconversion photoluminescence in two-dimensional materials

控和增强方式,最后展望二维材料体系激子上转换发光效应的应用前景。

2 上转换发光机制

根据能量守恒定律,在上转换发光过程中,如果入射激发光子能量较低,为辐射出更高能量光子,样品需要吸收额外的能量。额外能量来源主要包括声子(晶格振动)、多光子吸收、俄歇复合效应或者非线性效应等。上述能量来源构成了不同光学频率上转换发光机制,如声子辅助上转换发光、多光子吸收上转换发光、俄歇复合上转换发光等。

2.1 声子辅助上转换发光

作为晶格中原子集体振荡模式量子化所对应准粒子,声子一般情况下被认为是对发光有害的:声子会引起发光中心的重叠、电离和多声子非辐射弛豫^[27-30],从

而形成热淬灭,并减弱发光强度。但以某些特定频率入射时,声子的参与会显著增强发光强度,并且使出射光频率高于入射光,即声子辅助上转换发光。

在声子辅助上转换发光中,电子首先被一个低能量光子激发到一个虚拟或实际存在的中间态上,然后再吸收一个或多个声子跃迁到最终激发态并复合发光^[图 2(c)]。实际存在的中间态包括缺陷态、表面态等^[31-32]。当激发光的波长与实际中间态共振时,上转换发光会被显著增强^[33-34],根据此现象可以用光致发光(PL)激发光谱来进行缺陷态、表面态探测^[35]。由于实际的中间态和最终激发态固定,上转换发光频率不随入射光频率改变^[36]。但对反斯托克斯拉曼过程而言,其出射光光子能量等于入射光光子能量和一个振动模式能量之和,因此不论如何改变入射光的频率,拉曼过程产生的反斯托克斯光与入射光的频率差总是恒定^[31, 37]。

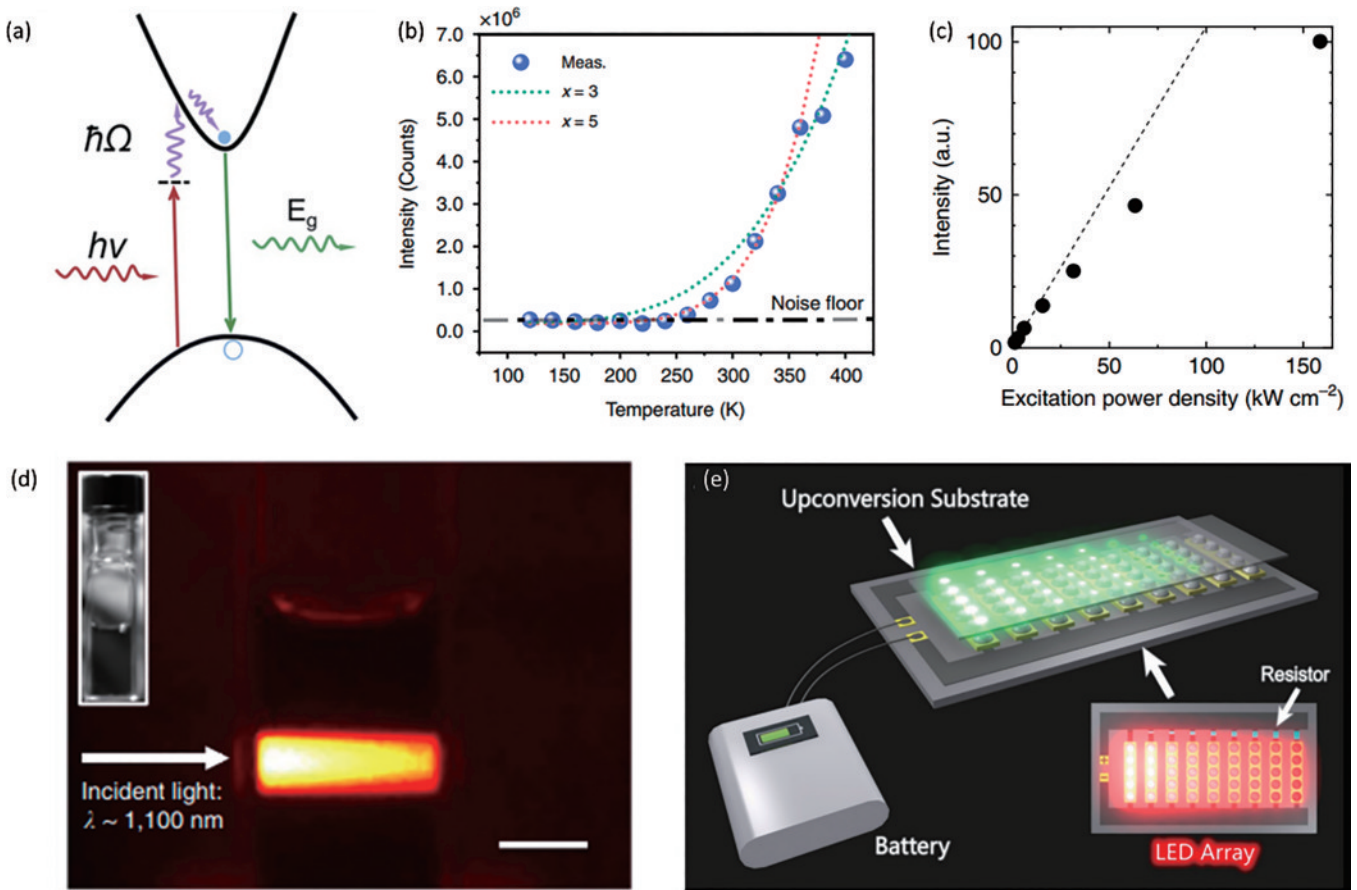


图 2 声子辅助上转换发光。(a) 声子辅助上转换发光机制示意图^[42]; (b) 声子辅助上转换发光的温度依赖特性,绿色和红色虚线分别为三声子和五声子过程拟合^[39]; (c) 声子辅助上转换发光的功率依赖特性,虚线为线性拟合^[31]; (d) 碳纳米管溶液中的声子辅助上转换发光实验现象图,插图为无入射光时碳纳米管溶液照片^[31]; (e) LED灯激发声子辅助上转换实验装置示意图^[41]

Fig. 2 Phonon-assisted upconversion photoluminescence. (a) Schematic illustration of the phonon-assisted upconversion photoluminescence mechanism^[42]; (b) temperature dependence of the phonon-assisted upconversion photoluminescence, where the green and red dashed lines represent the fitting for the three-phonon and five-phonon processes, respectively^[39]; (c) pump power dependence of the phonon-assisted upconversion photoluminescence, with the dashed line showing a linear fit^[31]; (d) experimental observation of phonon-assisted upconversion photoluminescence from carbon nanotube solutions, with the inset showing a photo of the carbon nanotube solution without incident light^[31]; (e) diagram of the experimental setup for phonon-assisted upconversion excited by an LED lamp^[41]

声子辅助上转换发光的一个典型特征是其显著的温度依赖特性^[38]。温度越高,晶格振动越剧烈,声子数密度就越大,因此声子辅助上转换发生的概率增加。与此同时,由于温度越高非辐射弛豫越强,正常的下转换发光反而会被削弱。声子辅助上转换与温度的关系通常和上转换所需声子的数目有关。值得注意的是,如图 2(d)所示,对于多声子吸收的声子辅助上转换发光,随着温度升高,晶格膨胀导致最终发射光子能量红移,激发光子能量不变情况下,所需吸收声子数变少^[39]。

声子辅助上转换的另一个特征是,由于只需要一个光子参与上转换过程,声子辅助上转换发光的强度和光功率之间呈线性关系^[34, 36, 40]。如图 2(e)所示,在激发光功率较低时,上转换发光的强度几乎随激发光功率线性增长;当继续增加激发光功率时,由于最终的激发态饱和,上转换发光的功率会从线性增长减弱为亚线性增长^[31]。

其实验现象如图 2(a)所示。与多光子吸收上转换相比,声子辅助上转换需要的光强阈值很低,可以用

一台商用的低功率连续激光器,甚至一台近红外 LED 便可实现[图 2(b)]^[41]。

2.2 多光子吸收上转换发光

除了吸收额外声子,吸收额外光子同样可以实现上转换发光效应,即多光子吸收上转换。如图 3(a)^[42]所示,多光子吸收上转换发光是指样品同时或先后吸收多个光子到达最终的激发态,并复合出射一个高能量光子过程,其实验现象如图 3(b)所示。一步吸收多个光子过程被称为相干多光子吸收,只需要虚拟中间态;而先后吸收多个光子过程被称为多步吸收,需要实际的中间态方可完成。按照能量守恒定律,最终出射的光子能量小于等于吸收多个光子能量的加和。由于多光子吸收是非线性过程(对 n 个光子的吸收是 $2n-1$ 阶非线性过程^[43]),其需要的入射光强阈值要远大于声子辅助上转换。双光子和三光子是比较常见的多光子吸收过程^[44-45],也有高达 5 个光子的多光子吸收上转换被报道^[46]。此处以最常见双光子吸收为例讨论多光子吸收上转换发光物理机制。

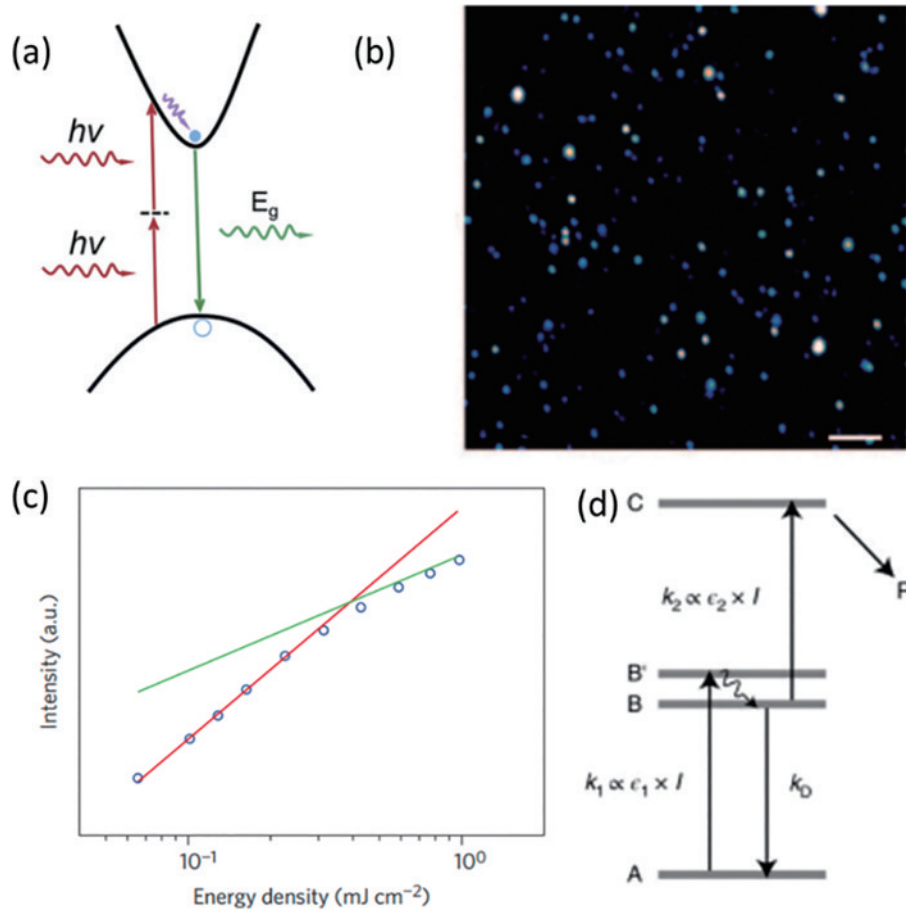


图 3 双光子上转换发光。(a) 双光子上转换发光机制示意图^[42]; (b) 多光子吸收上转换发光实验现象^[45]; (c) 双光子上转换的功率依赖特性, 红线为二次方拟合, 绿线为线性拟合^[49]; (d) 两步吸收上转换发光机制示意图^[52]

Fig. 3 Two-photon upconversion photoluminescence. (a) Schematic illustration of the two-photon upconversion photoluminescence mechanism^[42]; (b) multi-photon absorption upconversion photoluminescence phenomenon^[45]; (c) pump power dependence of the two-photon upconversion photoluminescence, with the red line showing a quadratic fit and the green line showing a linear fit^[47]; (d) schematic illustration of the two-step absorption upconversion photoluminescence mechanism^[52]

在相干双光子吸收过程中,基态的电子通过一个虚拟中间态,同时吸收两个低能量的入射光子,被激发到最终激发态并与空穴复合发光。由于虚拟中间态寿命极短,并且是相干激发,因此需要高峰值功率且相干脉冲激光光源才可以实现比较高效的相干双光子上转换^[32, 47-48]。除了需要高峰值功率光源外,另一个可以区分双光子吸收与声子辅助吸收的特征是:双光子吸收上转换发光的光功率与激发光功率呈二次依赖关系^[47],而声子辅助上转换为线性依赖关系。由于最终激发态上可供占据的电子态是有限的,当激发光强超过饱和强度时,如图 3(c)所示,二次依赖关系无法维持,上转换发光的光功率随激发光功率增加减缓,出现饱和^[49]。

由于相干双光子上转换需要能量较强,在上转换过程中可能伴随其他非线性过程,如三光子吸收^[50-51];此外,高激发阈值使其必须使用飞秒脉冲激光器才能实现,也增加了系统成本,并降低了系统集成度,因此两步吸收过程由于其低激发阈值在三维打印等领域也引起了广泛的研究兴趣^[52]。两步吸收具体过程是,基态的电子首先吸收一个光子,被激发到一个实际的中间态上,然后再吸收一个光子跃迁到最终的激发态上,并与空穴复合产生荧光[图 3(d)]。两步吸收上转换

效率主要由激发截面决定,包括中间态的激发截面和最终态激发截面,此外还受中间态的态密度和寿命影响^[48, 53]。由于中间态的寿命相当长,大约为纳秒级或更长时间,低功率连续波激光便可实现两步双光子吸收^[48]。

2.3 俄歇复合上转换发光

与前两种上转换方式只需要一个电子和一个空穴参与不同,俄歇复合上转换需要多个电子/空穴参与。最典型的俄歇复合上转换发光如图 4(a)所示,两个电子各吸收一个低能量电子被激发至中间态,然后其中一个电子与空穴复合,释放的能量被另一个电子吸收,把它激发到更高能级,从而完成上转换激发^[54-55]。由于需要更多电子/空穴参与,俄歇复合上转换通常发生于异质结、量子点等有异质边界地方,这是因为在异质边界处电子、空穴被注入,从而更易实现俄歇复合^[56-58]。

此外,在二维材料中存在另一种由激子效应引发的俄歇复合上转换。不同之处在于,电子不是与空穴复合,而是与空穴通过库仑作用形成束缚态的激子,由此释放的能量把另一个电子激发到最终能级,如图 4(b)^[59]所示。由于二维材料中激子束缚能很强,即使在室温下也可以产生激子^[60],因此这类上转换过程在二维材料中较为常见。

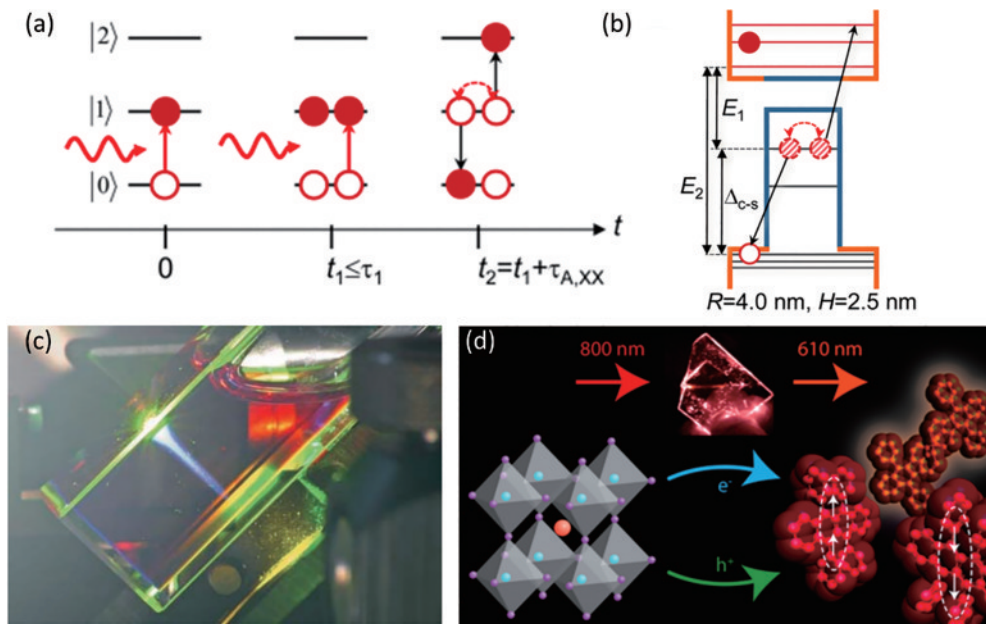


图 4 俄歇复合上转换发光。(a) 俄歇复合上转换发光机制示意图^[42]; (b) 激子效应引发的俄歇复合上转换示意图^[59]; (c) 有机材料中的三重态-三重态湮灭上转换发光现象^[64], 激发光为太阳光中的绿光部分, 有机材料为金属卟啉大环(MOEP)与聚五苯混合物; (d) 二维材料与有机材料界面中的三重态-三重态湮灭上转换发光机制示意图^[66], 二维钙钛矿中被入射光激发的自由电子和空穴转移到红荧烯中, 发生三重态-三重态湮灭上转换发光

Fig. 4 Auger recombination assisted upconversion photoluminescence. (a) Schematic illustration of the Auger recombination assisted upconversion photoluminescence mechanism^[42]; (b) schematic diagram of the exciton-induced Auger recombination assisted upconversion^[59]; (c) triplet-triplet annihilation upconversion photoluminescence in organic materials^[64], with the excitation light being the green component of sunlight and the organic material being a mixture of metalloporphyrin (MOEP) and pentaphenyl; (d) schematic illustration of the triplet-triplet annihilation upconversion photoluminescence mechanism in interface between two-dimensional materials and organic materials^[66], where the free electrons and holes excited by the incident light in the two-dimensional perovskites transfer to the rubrene and undergo triplet-triplet annihilation upconversion

还有一种俄歇复合上转换,被称为三重态-三重态湮灭。在此类上转换过程中,两个电子同时被激发到三重态,然后其中一个电子从三重态回到单重态释放的能量把另一个电子激发到更高的三重态^[61]。由于有机材料中有较为丰富的三重态和单重态能级,因此这种上转换过程通常发生于有机材料中[图 4(c)]^[62-64],也可发生在与有机材料接触的二维材料中[图 4(d)]^[65-66]。

3 二维材料体系上转换发光

目前的研究中,已经在二维 hBN、单层过渡金属二硫化物(TMDCs)、二维钙钛矿等二维材料中观察到了上转换发光现象,在本节中将对这些研究的内容进行回顾。

3.1 TMDC 单层材料

石墨烯作为第一种被发现的二维材料获得了巨大成功。尽管石墨烯具有优秀的电、热、光和机械性能,但由于其零带隙的限制,其在各种电子和光电子器件的应用上具有固有局限,启发人们开始寻找具有非零带隙的二维半导体材料^[67-68]。过渡金属二硫化物 TMDCs 是一类层状材料,最常见的 TMDC 材料主要有 MoS₂、WS₂、MoSe₂ 和 WSe₂,其结构如图 5(a)所示,过渡金属原子层夹在两个硫族原子层之间,通过共价键和范德瓦尔斯力分别维持平面内和层间稳定性。由于晶体层间较弱的范德瓦尔斯力作用,可以通过机械剥离方法制备高质量单层。层间相互作用减少会导致价带下移,体材料到单层会由间接带隙半导体转变为直接带隙半导体。与其他二维材料相比^[69-70],由于其带隙为 1~3 eV,集中在人们常用的可见光与红外波段,且具有较强的光致发光发射率,受到了研究者的广泛关注^[67-68, 71]。TMDCs 材料的另一个独特优势是材料中声子可以匹配两个激子态的能量差,实现声子辅助上转换过程的共振激发^[72]。

TMDC 材料中丰富的激子态和强电子-声子相互作用使其可通过多种机制实现上转换发光效应。首先,单层 TMDC 材料中声子辅助上转换现象可以通过一个真实的中间态发生,比如缺陷态^[33]、带电激子态^[34, 36, 73-74]或激子基态^[75]。在所有 TMDC 材料中,WS₂ 单层具有相对较高的发射量子效率,因此上转换发光的概率较高^[33]。Wang 等^[33]报道了通过多声子吸收实现的 WS₂ 单层的上转换发光,其光谱如图 5(b)所示。中间态被认为是被氧气吸附的硫二空位缺陷态[图 5(c)]。该研究实现了室温(300 K)条件下最高 219 meV 的光子能量增益,远高于室温热涨落能(26 meV)以及 WS₂ 单层的一阶和四阶拉曼模式的能量(21.7~86.9 meV),说明上转换过程是通过多声子吸收来实现的。

除了缺陷态,带电激子态也可作为真实中间态实现光子上转换效应^[34, 36, 73-74]。如图 5(d)所示,低温下

光致发光光谱揭示了单层 WS₂ 中单重态带电激子能级、三重态带电激子能级、中性激子能级分布情况。改变激发波长,跨越三重态能级,会在带电激子态能量处出现共振上转换峰值^[34, 36, 73-74],偏离带电激子态将降低上转换效率[图 5(e)]。2016 年 Jones 等^[34]首次报道了单层 WSe₂ 中基于带电激子态的声子辅助上转换,如图 5(f)所示,入射光子与带电激子态共振,出射光子与中性激子态共振,出射/入射光子能量差达到 30 meV。由于此能量差正好与单层 WSe₂ 中 A' 光学声子的能量相同,因此被认为发生了双共振的声子辅助上转换^[34]。2019 年 Jadcak 等^[36]也在 WS₂ 中发现了带电激子-激子双共振的多声子吸收辅助上转换发光[图 5(g)],出射/入射光子能量差可达到 150 meV,与三个 A' 声子振动能量所对应的 156 meV 相匹配,因此可认为有三个声子吸收参与该过程。值得注意的是,由于出射光子能量一般随温度降低而蓝移,出射/入射光子能量差可通过调控激发光子能量和温度来实现,随着出射/入射光子能量差增大,上转换发光强度指数衰减[图 5(h)]。

除此之外,激子基态也可作为上转换中间态。Manca 等^[75]报道了一个以基态(A:1s)为中间态上转换到激子激发态(A:2s)的声子辅助上转换发光,如图 5(i)所示,出射/入射光子能量差达到 133 meV。由于该实验在 4 K 温度下进行,理论上声子的数目应该很少,但研究者认为声子可以从经过双光子吸收或激子到带电激子转换后热电子的弛豫中生成^[75]。

如前文所述,双光子吸收上转换可以通过虚拟的中间态进行相干双光子吸收,也可以通过实际的中间态进行两步吸收。2015 年, Xiao 等^[77]报道了通过 WS₂ 单层中的虚拟态进行的双光子吸收上转换现象[图 6(a)],当两倍激发光子能量与激子 2p 能级达到共振时,上转换效率最高。时间分辨荧光测量结果表明,在双光子激发后,从 2p 态到 1s 态的弛豫时间为 600 fs,从 1s 态到价带的复合时间为 5 ps[图 6(b)]。使用圆偏振激发的检测方法,估计出谷间散射寿命为 3 ps,随后复合寿命为 8.3 ps[图 6(c)]。对于双光子上转换,谷极化仍然存在。在激发能量为 1.13 eV 时,谷极化率可达 29.6%。当将两倍的激发能量偏离激子 2p 能级时,极化率逐渐降低[图 6(d)]。这种双光子激发激子谷间动力学的研究对于非线性光学体系中操纵谷自由度至关重要。

2017 年, Lundt 等^[78]把 MoSe₂ 单层材料[图 6(e)]嵌入到如图 6(f)所示的微结构中,观察到了两步吸收双光子上转换发光。在这种结构中金纳米层附近光场被分布布拉格反射镜和金纳米层构成的 Tamm 结构显著增强[图 6(g)],腔内光场与 MoSe₂ 单层材料中的带电激子态强耦合,产生了两个带电激子-极化子分支,如图 6(h)所示。在用连续光激光器激发能量较低的带电激子-极化子分支时,能量较高的带电激子-极

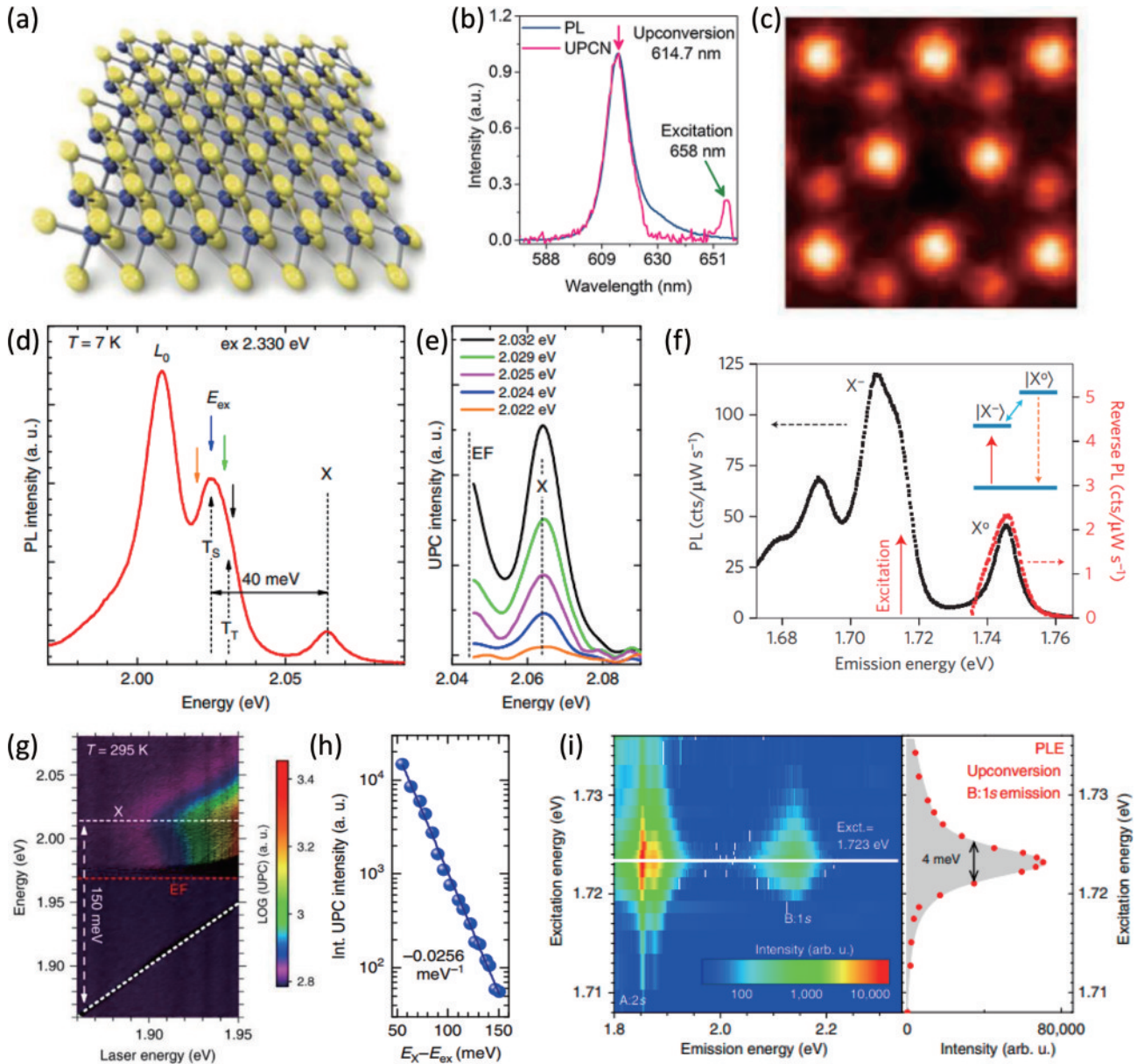


图 5 单层 TMDC 中的声子辅助上转换发光。(a) TMDC 原子结构示意图^[76]；(b) 单层 WS₂ 的上转换发光 (粉色) 与正常发光 (绿色) 的光谱对比^[33]，上转换发光和正常发光的激发光波长分别为 658 nm 和 532 nm；(c) 通过透射电子显微镜获得的单层 WS₂ 材料中的硫缺陷态照片^[33]；(d) 单层 WS₂ 的光致发光光谱，其中 T_s 为单重态带电激子能级， T_T 为三重态带电激子能级，X 为中性激子能级^[34]；(e) 单层 WS₂ 在不同频率激发光下的上转换光谱，激发光频率以对应颜色标注在 (d) 中^[34]；(f) 单层 WSe₂ 的光致发光光谱 (黑色) 和上转换发光光谱 (红色)，插图为声子辅助上转换发光原理示意图^[34]；(g) 单层 WS₂ 中上转换发射光谱随激光激发光子能量的变化，环境温度为 295 K^[36]；(h) 上转换发光积分强度与出射/入射光子能量差之间的关系^[36]；(i) 左图为 WS₂ 中上转换发光光谱的等高线图，入射光与 A:1s 态共振，右图显示共振的半峰全宽为 4 meV^[75]

Fig. 5 Single-photon upconversion photoluminescence in single-layer TMDCs. (a) Schematic diagram of the atomic structure of TMDCs^[76]; (b) comparison between upconversion photoluminescence (pink) and normal photoluminescence (green) spectra of a monolayer WS₂^[33], the excitation laser wavelengths for upconversion photoluminescence and normal photoluminescence are 658 nm and 532 nm, respectively; (c) image of sulfur vacancy states in monolayer WS₂ material^[33]; (d) photoluminescence spectrum of single-layer WS₂, where T_s is the spin-triplet charged exciton state, T_T is the spin-triplet neutral exciton state, and X is the neutral exciton state^[34]; (e) upconverted photoluminescence spectra of single-layer WS₂ under excitation at different frequencies as labeled by corresponding colors in Fig. (d)^[34]; (f) photoluminescence spectrum (black) and upconverted photoluminescence spectrum (red) of single-layer WSe₂, the inset shows a schematic of the phonon-assisted upconversion process^[34]; (g) evolution of the upconversion emission spectra as a function of the laser excitation photon energy in monolayer WS₂, recorded at 295 K^[36]; (h) dependence of the upconversion integrated intensity on the energy difference of the neutral exciton and the excitation photon energy^[36]; (i) left panel is contour plot of the upconversion photoluminescence spectra in WSe₂ with the incident light resonant with the A:1s state, and right panel is full width at half maximum of the resonance is 4 meV^[75]

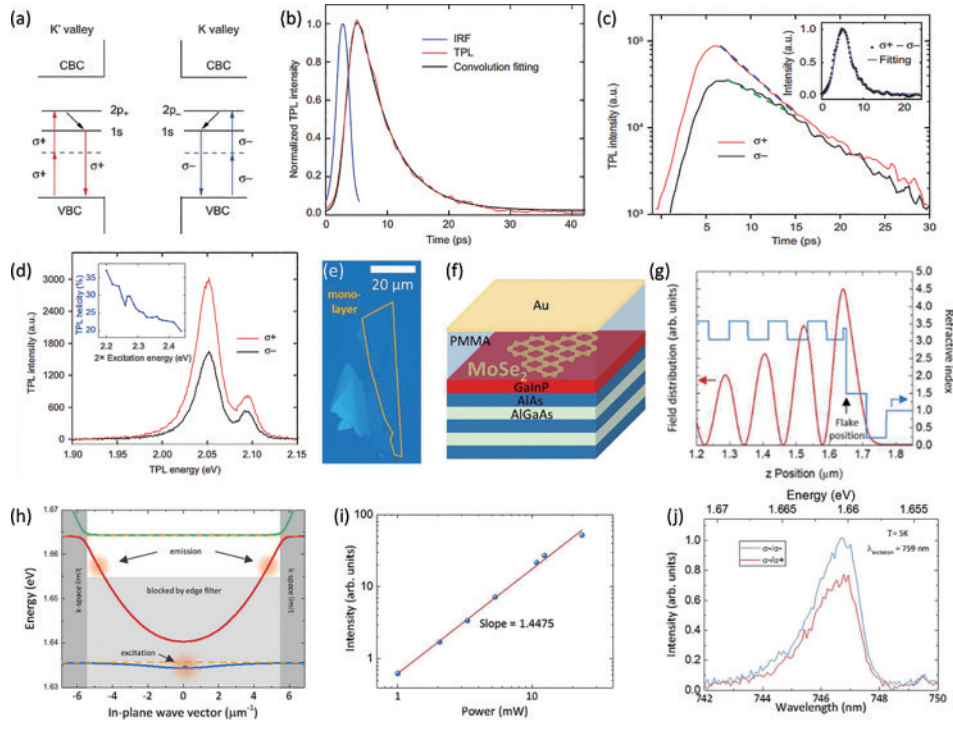


图 6 单层 TMDC 中的双光子上转换发光。(a) 双光子上转换的谷极化示意图,在 K 和 K' 谷表现为相反的自旋^[77]; (b) 被线偏振的 1.13 eV 脉冲光激发的双光子上转换发光(红色)的时间演化曲线^[77]与仪器响应函数(蓝色)对比,双光子上转换时间演化曲线展现出明显的上升和衰减特征。基于三能级速率方程模型卷积拟合,交互激子松弛时间 $\tau_{2p-1s} = (600 \pm 150)$ fs,复合时间 $\tau_{rec} = (5.0 \pm 0.2)$ ps[]]; (c) 由 1.13 eV 的 $\sigma+$ 偏振光激发的双光子上转换发光的时间演化曲线^[77] [由于选择规则和谷间散射,相比 $\sigma-$ 发射(黑曲线), $\sigma+$ 发射(红色)显示出更高的强度和更快的衰减。蓝色和绿色虚线是指数拟合。插图展示了时间分辨的谷激子集居数($\sigma+ - \sigma-$, 黑点)的卷积拟合(紫色)。弛豫时的谷间散射时间 $\tau_{inter(2p-1s)}$ 和复合时的谷间散射时间 $\tau_{inter(1s)}$ 被估计分别为 (3 ± 1) ps 和 (8.3 ± 0.5) ps。误差范围是从对多次重复测量结果的拟合中获得的]; (d) 在 $\sigma+$ 光激发下,检测 $\sigma+$ (红色)和 $\sigma-$ (黑色)激发光下的双光子上转换发光偏振^[77] [根据多次重复测量,观察到了 $P = 29.6\% \pm 0.5\%$ 的圆偏振率,激发光能量为 1.13 eV。插图绘制了在 $\sigma+$ 偏振光激发下,扫描相同范围的双光子上转换偏振率与激发能量之间的关系]; (e) 转移到光子微结构上的单层 MoSe₂ 显微镜照片^[78]; (f) 嵌入单层 MoSe₂ 的光子微结构示意图^[78]; (g) Tamm 微结构中的折射率分布(蓝色)和光场强度分布(红色)^[78]; (h) 光子微结构中带电激子-极化子的色散关系,其中圆点表示激发光和出射光在色散关系中的位置,灰色阴影表示由边缘滤波和数值孔径造成的探测界限^[78]; (i) Tamm 微结构上单层 MoSe₂ 上转换发光的功率依赖关系^[78]; (j) 在 $\sigma-$ 偏振光激发下出射的 $\sigma+$ (红色)和 $\sigma-$ (蓝色)光强^[78]

Fig. 6 Upconversion photoluminescence in single-layer TMDCs. (a) Schematic of the valley polarization in two-photon upconversion, showing opposite spins in K and K' valleys^[77]; (b) time trace of the two-photon upconversion photoluminescence (red curve) excited by a linearly polarized 1.13 eV pulse laser^[77] [compared with the instrument response function (blue curve), the upconversion time trace exhibits observable rising and decaying features. Based on the convolution fitting using a three-level rate equation model, the interexciton relaxation time $\tau_{2p-1s} = (600 \pm 150)$ fs and the recombination time $\tau_{rec} = (5.0 \pm 0.2)$ ps[]]; (c) time traces of the two-photon upconversion photoluminescence excited by 1.13 eV $\sigma+$ polarized light^[77] [due to the selection rules and intervalley scattering, the $\sigma+$ emission (red curve) displays higher intensity and faster decay compared to the $\sigma-$ emission (black curve). The blue and green dashed lines are exponential fits. The inset shows the convolution fit (purple) for the time-resolved valley exciton population ($\sigma+ - \sigma-$, black dots). The intervalley scattering times during relaxation, $\tau_{inter(2p-1s)}$, and recombination, $\tau_{inter(1s)}$, are estimated to be (3 ± 1) ps and (8.3 ± 0.5) ps, respectively. The error ranges were obtained from fitting to the results of multiple repeated measurements]; (d) polarization-resolved two-photon upconversion photoluminescence measurements for $\sigma+$ (red curve) and $\sigma-$ (black curve) polarization under $\sigma+$ light excitation^[77] [circular polarization of $P = 29.6\% \pm 0.5\%$ was observed based on multiple repeated measurements at an excitation energy of 1.13 eV. The inset plots the upconversion photoluminescence helicity versus the excitation energy for a scan of the same range under $\sigma+$ polarized excitation]; (e) schematic of the photonic structure with embedded single-layer MoSe₂^[78]; (f) microscope image of the investigated MoSe₂ monolayer transferred onto the bottom DBR structure^[78]; (g) refractive index profile (blue) and electric field intensity distribution (red) in the Tamm microcavity structure^[78]; (h) dispersion relation of charged exciton-polaritons in the photonic structure, dots indicate the position of excitation and emission light in the dispersion, the shaded area shows the detection limit imposed by edge filtering and numerical aperture^[78]; (i) power dependence of the upconverted photoluminescence from monolayer MoSe₂ on the Tamm microcavity structure^[78]; (j) emitted $\sigma+$ (red) and $\sigma-$ (blue) intensities under $\sigma-$ polarized excitation^[78]

分子分支的光子被探测到,结合功率依赖曲线[图 6(i)],拟合得到的幂指数为 1.4475,认为声子辅助上转换和双光子上转换共同参与了上转换发光过程,结合对圆偏振度的测量[图 6(j)],认为声子辅助上转换占主导。这项研究展示了在强耦合状态下实现双光子吸收的新路径。

在 hBN 封装 MoS_2 、 WSe_2 、 MoSe_2 和 MoTe_2 单层中,还可通过从激子基态到激发态的俄歇复合实现上转换^[75, 79]。对 MoSe_2 单层激子基态 A:1s 的共振激发导致了显著的上转换发光效应,出射光与 A:2s 和 B:1s 共振,并且能量增益约为 200 meV。A:1s 态的下转换的综合光致发光强度呈次线性增长($\alpha=0.88$),随着激发功率的增加而增加。相比之下,上转换(A:2s+B:1s)的综合发光强度表现出超线性($\alpha=1.64$)对激发功率的依赖关系^[64]。上转换的激发功率指数约为下转换的两倍,说明上转换过程中需要两个基态激子。因此,俄歇复合上转换是最合理的机制。Han 等^[79-80]同时建立了理论模型来验证上转换的机制是俄歇复合,而不是两步双光子吸收,根据模型,共振俄歇复合上转换效率比两步双光子吸收效率高三个数量级。TMDC 单层中俄歇复合上转换效率显著增强主要来自于两方面:一是强库仑相互作用,使得单电子动量守恒弛豫成为可能;二是存在激发的导带,电子可以相对较小波矢轻松跃迁到其中。同时,这也说明俄歇复合上转换是探测 TMDC 单层中激发激子态的途径之一。

3.2 二维钙钛矿材料

二维钙钛矿材料[图 7(b)]具有低非辐射复合率^[81]、低激子束缚态能量^[82]、长载流子寿命^[83]等优良性质。化学式一般为 ABX_3 ,原子结构如图 7(a)所示,其中:A 代表有机阳离子,如甲基铵(MA)或甲氨基甲酸二铵(FA);B 代表二价金属,如铅或锡;X 代表卤素,如溴或碘^[80]。自从 2009 年首次被制造出来,用二维钙钛矿制造的光伏电池的光电转换效率已经由 3.8%^[84]激增至 25.2%^[85]。

二维钙钛矿材料优异的光学性质使其在上转换发光领域也具有巨大潜力。2016 年,Ha 等^[86]在二维钙钛矿中实现了声子辅助上转换发光,并用 180 W 的激发功率实现了 58.7 K 的光学制冷。研究者首先测量了光致发光光谱随温度变化[图 7(c)],发现光致发光谐振峰会随温度降低而蓝移,并以此作为探测二维钙钛矿材料温度手段;随后将吸收曲线与光致发光谱对比[图 7(d)],比谐振峰频率更高的一侧仅有较弱的光学吸收,在这个频率区域内由于出射光子能量大于激发光子能量,可以带走体系内的大量声子,有望实现光学冷却。随后以 632 nm 激发光入射,并实现了约 386 meV 能量增益的声子辅助上转换发光[图 7(e)]。通过控制激发光源的打开与关闭,观察到光致发光光

谱谐振峰的蓝移与红移,证明通过上转换发光实现了光学制冷[图 7(f)、(g)]。由于二维钙钛矿材料中声子辅助上转换发光的外量子效率超过 99%,在激光制冷过程中展示出优异的性能,因此受到研究者的广泛关注。

2017 年,Liu 等^[87]在二维钙钛矿中实现了双光子上转换发光[图 7(h)],双光子吸收系数达 211.5 cm/MW,比三维钙钛矿材料高一个数量级[图 7(i)]。2019 年,Nienhaus 等^[66]利用二维钙钛矿作为敏化剂,在红荧烯中实现近红外到可见光的三重态湮灭俄歇复合上转换发光,上转换效率达 3.1%。

3.3 2D-hBN 材料

二维六方氮化硼(2D-hBN)是一种宽禁带的二维半导体材料(带隙约 6 eV),其原子结构如图 8(a)所示,光学显微镜照片如图 8(b)所示。纯净的 2D-hBN 发光在紫外波段,但缺陷和应力的存在会在导带之下引入缺陷态,从而使其在可见光波段可以发光^[88-89]。h-BN 的缺陷态可以被应用于常温下的量子单光子源^[90],因此其缺陷态的上转换发光引起了研究者的广泛关注。由于 hBN 中的缺陷与晶格振动(声子)之间存在强耦合,h-BN 缺陷态呈现出较大的声子边带^[89]。声子与缺陷的强耦合为声子辅助上转换发光提供了有利条件^[91]。2018 年,Sahli 等^[85]报道了 2D-hBN 中的声子辅助上转换发光现象。用 610 nm 连续激光器照射时,出射光频率为 565 nm[图 8(c)],且上转换与下转换关于零声子线对称[图 8(d)],因此认为是吸收一个声子引发的上转换过程。同时通过理论计算 2D-hBN 中的各种缺陷对应的缺陷态能级表明,文中的声子辅助上转换发光可能来自于 B 空位或者 N 空位缺陷态[图 8(e)、(f)]。2019 年,Tran 等^[90]研究了 2D-hBN 中的声子辅助上转换对量子光源时域抖动的影响。研究者首先用 637 nm 的连续激光入射,得到中心波长约为 600 nm 的声子辅助上转换发光[图 8(g)],随后研究了声子辅助上转换发光和光致发光光谱的时间序列对比[图 8(h)、(i)]。由于声子辅助上转换所需激发光子能量低于缺陷态的带隙,被缺陷态俘获的电子也会更少地被激发和转移,从而抑制了缺陷态附近电子集聚产生的局域化电场导致的随机失谐,进而抑制了光谱扩散效应,因此声子辅助上转换发光可以有效地降低 2D-hBN 缺陷态量子光源的时域抖动。同时演示了 2D-hBN 中声子辅助上转换发光在发光波长选通方面的应用,通过交替激发光致发光和上转换发光[图 8(j)],实现了出射光波长在 600 nm 和 605 nm 之间的可控跃变[图 8(k)、(l)],在量子通信系统和波长复用系统中有潜在应用价值。

除了声子辅助上转换发光,2D-hBN 中缺陷态双光子上转换发光也有报道^[92]。首先用共聚焦显微镜确定缺陷的位置,然后用 780 nm 的脉冲激光对缺陷进行激发,得到 670 nm 的发射峰。由于出射光子数与入射

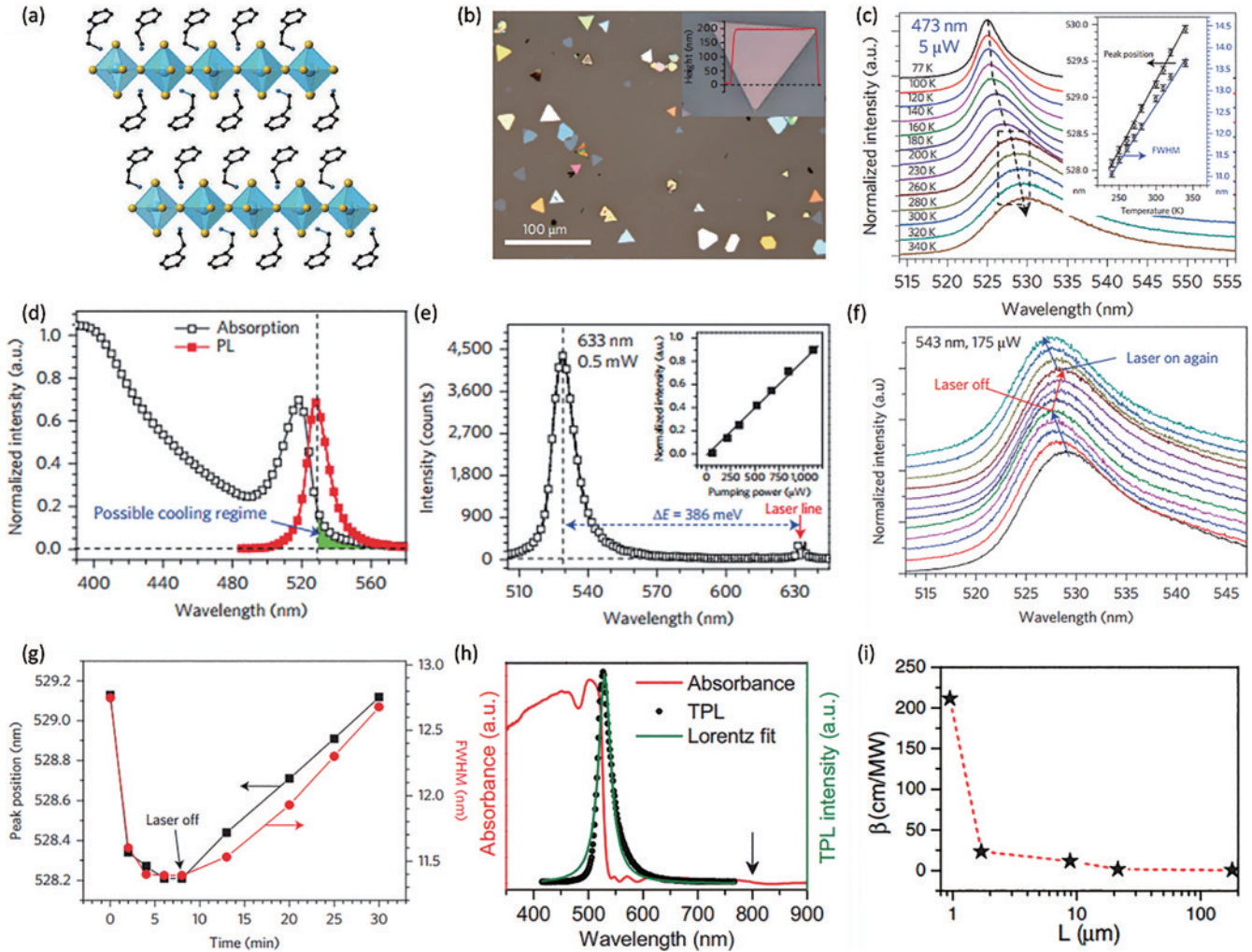


图 7 二维钙钛矿中的上转换发光。(a) 二维钙钛矿的原子结构, 蓝色球为 B, 黄色球为 X, 黑色链状结构为 A^[87]; (b) 二维钙钛矿材料的光学照片^[86], 插图为原子力显微镜扫描的高度空间分布, 证明所研究的材料是单层结构; (c) 光致发光光谱随温度的变化, 插图为提取的谐振峰中心频率和半峰全宽随温度变化^[86]; (d) 二维钙钛矿材料的吸收曲线(黑色)和光致发光光谱(红色)^[86], 绿色区域为有实现光学制冷潜在可能的区域; (e) 二维钙钛矿材料中的声子辅助上转换发光^[86], 能量增益为 386 meV [插图为出射光功率的能量依赖关系, 线性的能量依赖关系证明发生了声子辅助上转换发光]; (f) 打开和关闭激发光源时的泵浦-探测光学测温曲线, 红移和蓝移体现温度的上升与下降^[86]; (g) 从图(f)中提取的峰值对应波长(黑色)和半峰全宽(红色)变化^[86]; (h) 二维钙钛矿材料中的双光子上转换发光^[87]; (i) 双光子上转换系数与二维钙钛矿层数的关系^[87]

Fig. 7 Upconversion photoluminescence in two-dimensional perovskites. (a) Atomic structure of two-dimensional perovskites, with blue spheres representing B, yellow spheres representing X, and black chain representing A^[87]; (b) optical image of the two-dimensional perovskite material^[86], with the inset showing the height profile from atomic force microscopy scans, demonstrating the monolayer structure of the studied material; (c) temperature dependence of the photoluminescence spectra^[86], with the inset showing the extracted center frequency and full width at half maximum as a function of temperature; (d) absorption curve (black) and photoluminescence spectrum (red) of the two-dimensional perovskite material^[86], with the green shaded region indicating the potential region for optical cooling; (e) phonon-assisted upconversion photoluminescence in the two-dimensional perovskite material^[86], with an energy gain of 386 meV [inset shows the power dependence of the emitted light, and the linear dependence demonstrates the phonon-assisted upconversion]; (f) pump-probe optical thermometry curves when turning the excitation on and off, with the red and blue shifts indicating heating and cooling, respectively^[86]; (g) extracted peak wavelength (black) and full width at half maximum (red) from Fig. (f)^[86]; (h) two-photon absorption upconversion photoluminescence in the two-dimensional perovskite material^[87]; (i) relationship between the two-photon upconversion coefficient and the number of layers in two-dimensional perovskites^[87]

光功率呈二次方的功率依赖, 认为发生了双光子上转换发光。2D-hBN 中的双光子上转换发光现象在生物标记和非线性量子光学等领域有潜在应用价值, 并且为 2D-hBN 的缺陷态能带结构、量子效率和吸收截面

等特性的探测提供了新的手段。

为显示各二维材料上转换发光的性能, 表 1 对各种二维材料上转换发光的带隙及光子能量增益进行了对比。

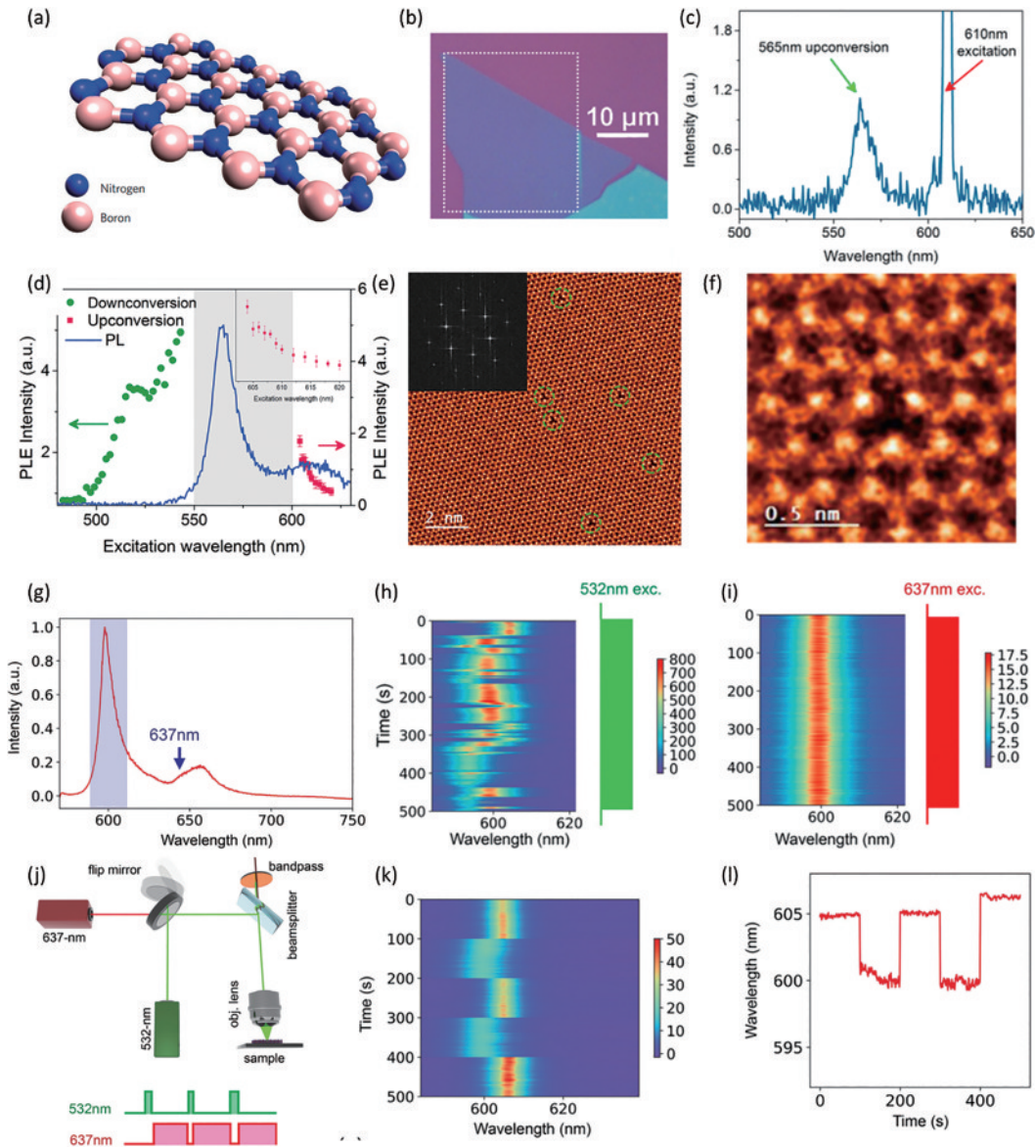


图 8 2D-hBN 中的上转换发光。(a) 2D-hBN 原子结构示意图^[88]；(b) SiO₂衬底上 2D-hBN 的光学显微镜照片^[91]；(c) 2D-hBN 中的声子辅助上转换发光^[91]；(d) 光致发光光谱(蓝色)和下转换(绿色)和上转换(粉色)的光致发光激发谱^[91] [阴影部分为测量光致发光激发谱时选择探测出射光的波长范围, 插图为放大的上转换光致发光激发谱]；(e) 2D-hBN 的扫描透射电子显微镜照片^[91], 绿色圆圈标出的为 B 空位(插图为显微镜照片的傅里叶变换)；(f) 放大的单个硼空位显微镜照片^[91]；(g) 2D-hBN 的光致发光谱^[90], 其中箭头指向位置为上转换发光效应的激发光波长, 阴影部分为测量上转换发光效应时选择的波长窗口范围；(h) 光致发光光谱的时间序列^[90]；(i) 上转换发光光谱的时间序列^[90]；(j) 发光波长选通装置示意图^[90](用振镜控制 532 nm 或 637 nm 光源入射, 从而选择性激发光致发光和上转换发光; 下半部分为 532 nm 和 637 nm 光源的时间序列图)；(k) 出射光光谱的时间序列^[90]；(l) 零声子线波长的时间序列^[90]

Fig. 8 Upconversion photoluminescence in 2D-hBN. (a). Schematic diagram of the atomic structure of 2D-hBN^[88]; (b) optical microscope image of 2D-hBN on a SiO₂ substrate^[91]; (c) phonon-assisted upconversion photoluminescence in 2D-hBN^[91]; (d) photoluminescence spectrum (blue) and photoluminescence excitation spectra for downconversion (green) and upconversion (pink)^[91] (shaded area indicates the wavelength range for detecting emitted light when measuring the excitation spectrum; the inset shows the enlarged upconversion excitation spectrum); (e) scanning transmission electron microscope image of 2D-hBN with B vacancies marked by green circles^[91] (inset shows the Fourier transform of the image); (f) enlarged microscope image of a single B vacancy^[91]; (g) photoluminescence spectrum of 2D-hBN^[90], where the arrow indicates the excitation wavelength for the upconversion effect and the shaded area indicates the wavelength window for measuring the upconversion; (h) time series of the photoluminescence spectra^[90]; (i) time series of the upconverted emission spectra^[90]; (j) schematic of the wavelength-selected excitation setup^[90] (532 nm or 637 nm source is switched by a flip mirror for selective excitation of photoluminescence and upconversion, the lower part shows time sequences of the 532 nm and 637 nm sources); (k) time series of the emitted light spectra^[90]; (l) time series of the zero-phonon line wavelength^[90]

表 1 二维材料带隙及上转换发光光子能量增益
Table 1 Bandgap energy and energy gain of PL upconversion in 2D materials

| Types of 2D material | Bandgap energy /eV | Energy gain of phonon-assisted upconversion /meV | Energy gain of two-photon PL upconversion /eV | Energy gain of Auger type PL upconversion /meV |
|----------------------|--------------------|--|---|--|
| TMDCs | 1-2 | 219 | 1.1 | ~200 |
| 2D-perovskites | 2 | 141.4 | 1.2 | ~420 |
| 2D-hBN | 6 | 100.0 | 0.26 | - |

4 二维材料上转换发光特性及调控

4.1 二维材料异质结中的上转换发光

二维材料异质结以单层二维材料为基本组成部分,由单层二维材料根据特定的顺序相互堆叠而成。单层二维材料中的强共价键提供了异质结的平面内稳定性,而相邻两层二维材料之间的范德瓦尔斯力提供了层间的稳定性。尽管层间的范德瓦尔斯力相对较弱,但二维异质结的物理特性严格取决于单层二维材料的堆积方向和层间距离,这为控制材料的响应提供了新的设计变量^[93-94]。目前已有报道在 MoSe₂/WS₂/MoS₂ 异质结^[95]和少层石墨烯/h-BN/WS₂ 异质结中^[96]的上转换发光,而其机制被认为是层间的电荷转移。

在图 9(a)和 8(b)所示的 MoSe₂/WS₂/MoS₂ 异质结中,两束 785 nm、670 nm 的入射光分别激发 MoSe₂ 和 MoS₂,使被激发的电子和空穴转移到 WS₂,并重新组合形成激子,最后复合发射出与 WS₂ 单层带隙能量相同的光子^[95]。研究者分别测量了上转换发光强度与两束光的功率依赖关系[图 9(c)],发现发光强度与 670 nm 光强呈线性关系,但与 785 nm 光强几乎独立,这是因为 670 nm 光可以同时激发 MoSe₂ 和 MoS₂ 使转移到 WS₂ 的电子和空穴数量同步增加,而 785 nm 光只能增加空穴数量不能增加电子数量,从而几乎不影响发光强度。为验证该猜想,研究者测试了分别只有 670 nm 和 785 nm 入射光的情况,如图 9(d)所示。在仅有 785 nm 光入射时,异质结未显示出上转换发光特性,而用 670 nm 光入射时出现了上转换发光效应,仅比两束光同时入射时发光强度减弱。分别单独改变 670 nm 和 785 nm 光强时的上转换发光光谱[图 9(e)、(f)]也支持这一判断。随后研究者分别测试了 WS₂、MoS₂ 和 WS₂/MoS₂ 异质结光致发光谱[图 9(g)],证明异质结中的激子复合发光来自 WS₂ 中的 A 激子。这项研究揭示了二维材料异质结中通过层间电子空穴转移导致的上转换发光新机制。

在少层石墨烯/h-BN/WS₂ 异质结[图 9(h)和 8(i)]中,也观察到了通过层间电荷转移实现的上转换发光^[96]。如图 9(j)所示,当正向栅压高于阈值时,WS₂ 层被正向栅压引入电子掺杂,光生空穴穿过 h-BN 屏障进入 WS₂ 单层,在 WS₂ 单层中形成激子,随后通过复合产生显著的上转换发光[图 9(k)]。除了上转换发光,这种混合器件中还检测到上转换光电流。在功率

为 5 mW、785 nm 激光(连续波)激发下,光电流测量值为 400 pA。如图 9(l)、(m)所示,上转换发光和光电流的强度均随入射激光功率线性增加,表明上转换是一个单光子激发过程。上述 2D 异质结光电器件上转换研究证实了实现新型电光上转换器件的可能性。

4.2 层数转角依赖的上转换发光

对三维体材料而言,当材料厚度增加时,理论上由于光与物质相互作用的长度增加,上转换发光也会相应增强^[97],由于层数对二维材料的物理性质的显著影响,二维材料厚度(即层数)对上转换发光的调控也更加复杂。以 MoS₂ 为例,随着层数增加,MoS₂ 会从直接带隙半导体过渡到间接带隙半导体,价带有效质量和电子迁移率也会发生明显变化^[98]。因此二维材料层数变化也会引起上转换发光特性的变化。2022 年, Duan 等^[65]用 MoSe₂ 和红荧烯组成如图 10(a)和 10(b)所示异质结,利用层间激子转移至红荧烯中进行三重态-三重态湮灭实现上转换发光。研究者用 772 nm 连续激光入射,观察到了约 660 nm 处的上转换发光现象[图 10(c)],其中上转换光致发光扫描图像如图 10(d)所示。上转换发光光强与 MoSe₂ 层数关系如图 10(e)所示,上转换发光强度随层数的增加而减弱,研究者认为由于 MoSe₂ 层数增加,层间激子转移至红荧烯中需经过更长的输运距离,输运过程与弛豫过程竞争导致上转换发光强度下降。

除了简单的层数变化,将二维材料以不同扭转角度堆叠,可以得到更加丰富可调的长程周期性结构,即摩尔超晶格^[99],并发展出了一门新的科学分支——转角电子学^[100]。转角作为一个新的自由度可以调控能带结构^[101],也产生了很多新奇的物理现象如摩尔激子^[102]、摩尔极化子^[103]等。Lin 等^[104]在转角堆叠的双层 WSe₂ 中观察到了俄歇复合上转换发光,且上转换发光的中心频率随转角角度变化,最大变换幅度可达 235 meV。中心频率变化的原因被归结为层间杂化导致的电子非局域化对能带结构的调控。上转换发光频率与转角之间关系[图 10(f)]为探测二维材料堆叠转角角度提供了一种潜在新方法。此外, Dai 等^[105]用两层 WSe₂ 转角 5.5° 相互堆叠组成摩尔超晶格[图 10(g)],观测到了声子辅助上转换发光的增强和光致发光的减弱[图 10(h)、(i)],并把不同转角时的上转换发光强度和普通光致发光强度进行了对比。研究发现,尽管在转角接近 0°(1.1°)和大角度旋转(13.8°)时上转换发光的

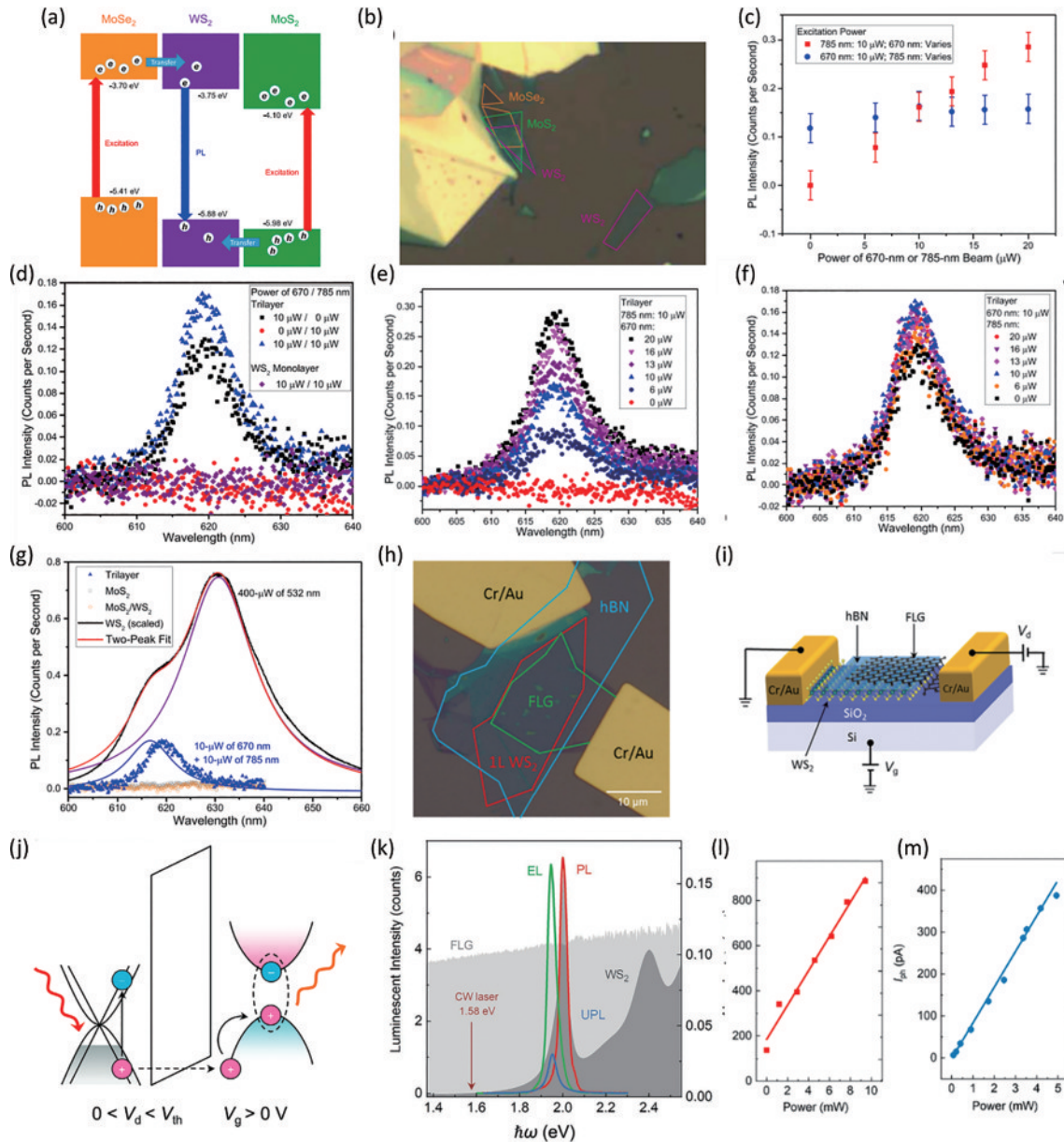


图 9 基于异质结对上转换发光的调控。(a) MoSe₂/WS₂/MoSe₂异质结上转换发光原理示意图^[95]；(b) 三层异质结结构和单层 WS₂ 结构的光学显微镜照片^[95]；(c) 上转换发光对激发光的功率依赖关系^[95]；(d) 单独用 670 nm (黑色)、785 nm (红色) 激发和两束光同时激发 (蓝色) 异质结的上转换发光, 以及单层 WS₂ 的上转换发光^[95]；(e) 改变 670 nm 激发光功率的上转换发光光谱^[95]；(f) 改变 785 nm 激发光功率的上转换发光光谱^[95]；(g) WS₂ (黑色), MoSe₂ (灰色) 和 WS₂/MoSe₂ 异质结 (橘色) 的光致发光谱, 和三层异质结结构的上转换发光光谱 (蓝色) 对比^[95]；(h) 异质结结构的光学显微镜照片^[96]；(i) 异质结结构示意图^[96]；(j) 少层石墨烯/h-BN/WS₂ 异质结上转换发光机制示意图^[96]；(k) 光致发光光谱 (红色), 栅压低于阈值的上转换发光光谱 (蓝色), 和栅压高于阈值的上转换发光光谱 (绿色)^[96]；(l) 上转换发光光强的功率依赖特性^[96]；(m) 光电流强度的功率依赖特性^[96]

Fig. 9 Manipulation of upconversion photoluminescence based on heterojunctions. (a) Schematic illustration of the upconversion photoluminescence mechanism in MoSe₂/WS₂/MoSe₂ heterojunctions^[95]; (b) optical microscope images of the trilayer heterostructure and monolayer WS₂ structure^[95]; (c) power dependence of the upconverted photoluminescence on the excitation power^[95]; (d) upconverted photoluminescence from the heterostructure excited by 670 nm (black), 785 nm (red) alone, both wavelengths simultaneously (blue), and from monolayer WS₂^[95]; (e) upconverted emission spectra as a function of 670 nm excitation power^[90]; (f) upconverted emission spectra as a function of 785 nm excitation power^[95]; (g) photoluminescence spectra of WS₂ (black), MoSe₂ (gray), WS₂/MoSe₂ heterostructure (orange), compared to the upconverted emission from the trilayer heterostructure (blue)^[95]; (h) optical microscope image of the heterostructure^[96]; (i) schematic diagram of the heterostructure^[96]; (j) schematic of the upconversion photoluminescence mechanism in few-layer graphene/h-BN/WS₂ heterostructure^[96]; (k) photoluminescence spectrum (red), upconverted emission below threshold gate voltage (blue), and above threshold gate voltage (green)^[96]; (l) power dependence of the upconverted emission intensity^[96]; (m) power dependence of the photocurrent intensity^[96]

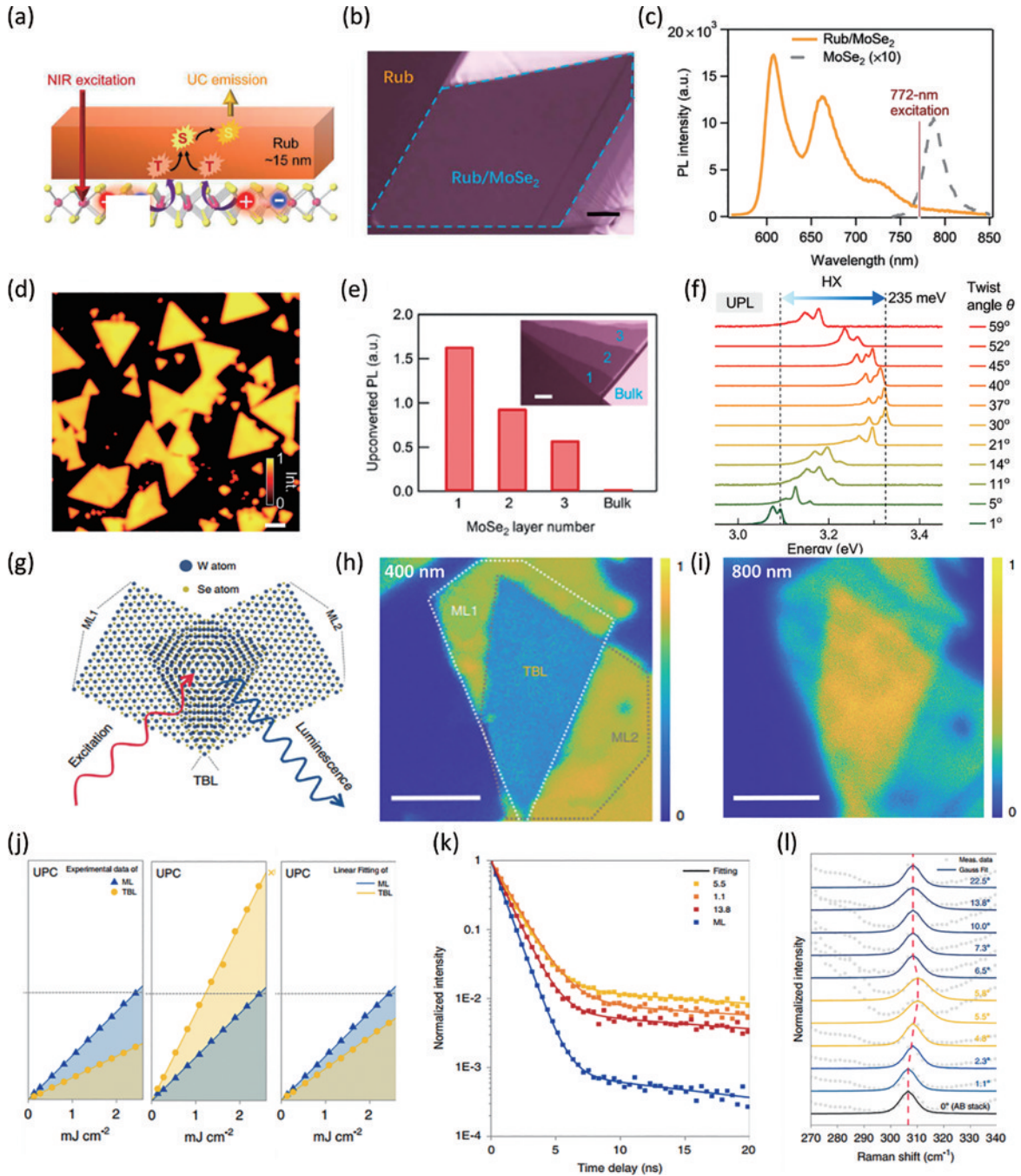


图 10 层数对上转换发光的调控。(a)单层 TMDC 材料与红荧烯界面的上转换发光示意图^[65];(b)单层 MoSe₂/红荧烯异质结光学显微镜照片^[65];(c)单层 MoSe₂/红荧烯异质结中的上转换发光光谱(橙色)和单层 MoSe₂的光致发光光谱(灰色)^[65];(d)单层 MoSe₂/红荧烯异质结中的上转换发光扫描图像^[65];(e)上转换发光强度与层数的关系^[65];(f)上转换发光光谱与转角的关系^[104];(g)转角堆叠二维材料结构示意图^[105];(h)转角堆叠二维材料光致发光扫描图像^[105];(i)转角堆叠二维材料上转换发光扫描图像^[105];(j)不同转角堆叠上转换发光与激发光强关系,以及和单层材料上转换发光的对比^[105];(k)通过泵浦探测实验测量不同转角下光致发光的弛豫时间^[105];(l)不同转角下的拉曼光谱频移^[105]

Fig. 10 Control of upconversion photoluminescence by number of layers. (a) Schematic of upconversion photoluminescence at the interface between monolayer TMDCs and rubrene ^[65]; (b) optical microscope image of monolayer MoSe₂/rubrene heterostructure^[65]; (c) upconversion spectrum (orange) from MoSe₂/rubrene heterostructure and photoluminescence spectrum (gray) from monolayer MoSe₂ ^[65]; (d) optical image of upconversion photoluminescence from MoSe₂/rubrene heterostructure^[65]; (e) upconversion intensity versus number of layers^[65]; (f) upconversion spectra versus twist angle^[104]; (g) schematic of twisted bilayer two-dimensional material structure ^[105]; (h) photoluminescence image of twisted bilayer structure^[105]; (i) upconversion photoluminescence image of twisted bilayer structure^[105]; (j) excitation power dependence of upconversion for different twist angles compared to monolayer ^[105]; (k) photoluminescence relaxation times at different twist angles measured by pump-probe experiments^[105]; (l) Raman spectral shifts at different twist angles^[105]

强度依然相比单层被抑制,但在旋转 5.5° 时上转换发光被显著增强了 4 倍,而普通的光致发光却被削弱了 50%,如图 10(j)所示,同时系统解释这种反直觉的衬度反转现象。利用超快激光泵浦探测[图 10(k)]和拉曼光谱[图 10(l)]等研究手段,这一现象被归因于 WSe_2 转角双层中光谱红移引起的上转换泵浦效率提高和晶格弛豫导致的层间激子转换效率降低的共同影响。作为转角 TMDCs 中的一种新现象,这一结果为揭示转角堆叠对二维材料半导体中上转换发光和光与物质相互作用的独特影响提供了新的视角。同时,这种转角堆叠增强技术可以与其他增强技术,如光学微腔、等离子体共振、量子点等叠加,实现更高效激子-声子-光子相互作用增强,助力多功能量子光源、人造激子晶体和高性能半导体激光器等一系列前沿应用。

4.3 微腔增强上转换发光

尽管二维材料有优异的光学性质,但由于其厚度仅有单原子级,与光相互作用的长度极短,因而光与物质相互作用的强度受到限制。微腔可以通过等离子体共振实现光与物质的强耦合,且可以通过调控其结构尺寸、形状和结构间距方便地调节共振波长,是二维材料上转换发光的理想增强手段,也因此受到了人们的广泛关注^[106-107]。Mueller 等^[108]将金纳米颗粒沉积到单层 WSe_2 上形成微腔[图 11(a)、(b)],并调整其尺寸使激发光与暗激子谐振[图 11(c)],得到了接近 100 倍的声子辅助上转换发光增强[图 11(d)],而将金纳米颗粒改进为非对称的十面体形状[图 11(f)],可以进一步提高上转换发光的增强倍数[图 11(e)]。

此外, Qi 等^[39]提出,通过一定的设计,也可以让微腔有两个共振频率并分别和上转换发光的入射光和出射光频率相匹配,从而进一步增强声子辅助上转换发光,其表面结构如图 11(g)所示,原理图如图 11(h)所示。等离子体谐振腔的结构如图 11(i)所示,用金层和金纳米棒构成了镜上纳米粒子的等离子体谐振腔,其共振模式分别为偶极子模式(共振频率 1.67 eV)和四极子模式(共振频率 1.52 eV)。注意其在金层、金纳米棒和单层 WSe_2 之间分别用氧化铝和有机材料隔离开,从而有效抑制了热电子的转移。Qi 等用这种方法实现了高达 3 个数量级的上转换发光增强,同时使发光的饱和阈值降低 3 个数量级[图 11(j)、(k)]。Qi 等认为等离子体谐振腔对系统的影响可归纳为三个方面:1)微腔作为一个天线可以提高出射光的方向性,从而在探测器数值孔径不变的前提下增强对光的收集作用[图 11(c)、(d)];2)微腔对光场的局域化可以导致微腔附近入射光和出射光的光场均增强约 40 倍,从而可以导致 3 个数量级左右的饱和阈值降低;3)共振腔中的珀塞尔效应使发光的自发辐射得到了增强。

5 应用

5.1 光学制冷

生活中很多例子都可以说明,光照下物体的温度会升高。然而,1929 年德国物理学家 Pringsheim^[1]提出物质与光相互作用可以实现冷却。随后朗道以入射辐射场和被辐射物质为孤立系统,对光学制冷的物理机制给出了完整的热力学解释^[109]。1978 年 Merlin 等^[110]观察到 YbS 中的多声子辅助上转换过程,进一步验证光学冷却的可能。与原子光学制冷只能冷却单个或少数原子不同,固体光学制冷可以降低整个材料的宏观温度,因此在制冷技术方面有着非常重要的应用前景^[111]。比如在集成电路中,随着电子元器件尺寸不断减小,密度不断提升,能耗密度也不断增大,热流密度伴随着能耗密度持续增加,热管理成为制约集成电路器件高频性能和可靠性的关键因素。考虑到光学制冷具有体积小、效率高、无振动干扰、无需制冷剂等众多优势,高效光学制冷有望满足未来信息领域高速集成器件严苛的制冷需求^[34]。

在半导体中,光学冷却过程由激子主导。2013 年, Zhang 团队^[5]报道了硫化镉(CdS)纳米带室温条件下降温 40 K、100 K 环境条件下降温 15 K 的净降温效果,如图 12(a)、(b)所示,在红色区域对应的波长激发即可实现光学制冷,这是二维 TMDCs 材料在光学制冷领域的一个重大突破。2016 年, Ha 等^[86]在二维钙钛矿中实现了声子辅助上转换发光,并用功率为 180 μW 的激发光在室温实现了 58.7 K 的光学制冷,器件结构如图 12(c)所示,制冷所需时间约为 10 min[图 12(d)]。Ha 等将这种制冷效应归因于二维钙钛矿超过 99% 的外量子效率[图 12(e)],并证明了二维钙钛矿材料在光学制冷领域的巨大应用潜力。2022 年, Zhang 团队^[26]在二维 WS_2 中实现了对纵向光学声子的冷却,并且得益于二维过渡金属二硫化物材料中电子-声子的强耦合,对声子的冷却即使在室温下也可以被观测到。这不仅实现了对二维材料中单一种类光学声子的调控,也为进一步实现光学制冷夯实了基础。

5.2 对电子亚能带的探测

上转换通常涉及一个真实或虚拟的中间态。如果涉及真实的中间态,共振激发该中间态将导致上转换强度显著增强。因此,光致上转换发光是揭示其他光学方法无法感知或探测的电子亚能带的有效手段。例如,当通过俄歇复合上转换共振激发 TMDC 单层的激子基态 ($A: 1s$) 时,观察到激子激发态 ($A: 2s$ 和 $B: 1s$)^[75, 79],注意此时的激子基态很难直接观测,因其上的电子会很快耦合到其他激子态中。除了激子的基态和激发态外,二维材料中还存在丰富的暗激子态。根据选择定则,这些角动量量子数不为 0 的暗激子态无法被线性吸收的光致发光直接激发,只能通过多光子过程激发,因此可以通过双光子上转换发光对光致发

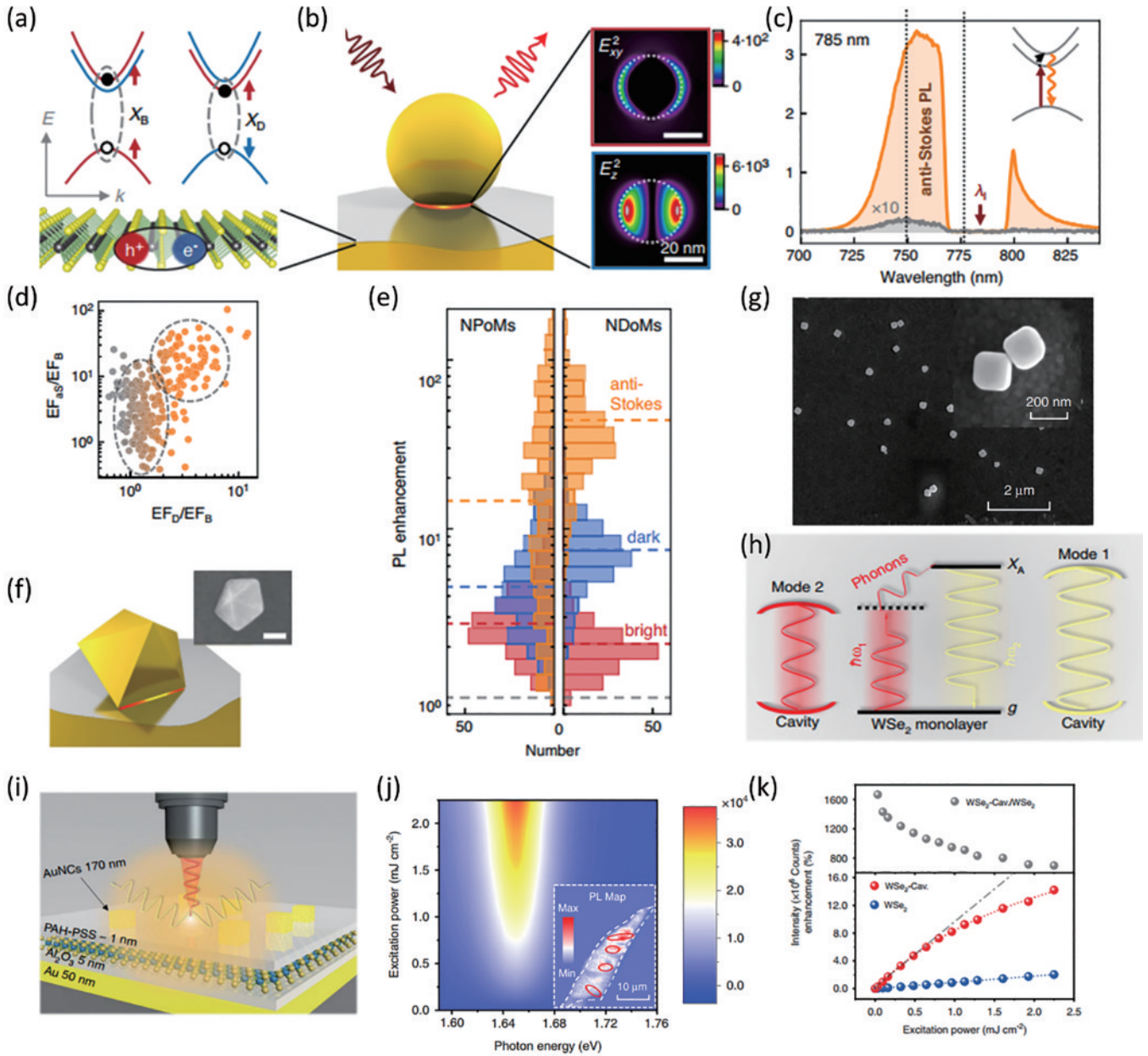


图 11 微腔增强上转换发光。(a) 二维材料中暗激子原理示意图^[108]；(b) 金纳米颗粒示意图^[108]，右图为仿真所得金纳米颗粒周边区域的光场分布；(c) 与暗激子共振的上转换发光光谱^[108]，插图为声子辅助上转换发光示意图；(d) 上转换发光增强系数与暗激子激发之间的关系^[108]，灰色区域表示暗激子很少被激发，橙色区域表示暗激子被激发；(e) 立方体微腔与纳米圆颗粒微腔增强效应对比^[108]；(f) 立方体微腔结构示意图^[108]；(g) 金纳米棒微腔结构示意图^[39]；(h) 双共振微腔增强原理示意图^[39]；(i) 双共振微腔结构示意图^[39]；(j) 上转换发光光谱的功率依赖，插图为微腔增强上转换发光的空间分布^[39]；(k) 上转换发光增强系数的功率依赖，下图为微腔增强上转换发光与未增强上转换发光的功率依赖对比^[39]

Fig. 11 Enhancement of upconversion photoluminescence by microcavity. (a) Schematic of dark excitons in two-dimensional materials^[108]; (b) schematic of gold nanoparticles^[108], with the right image showing the electric field distribution around the nanoparticles from simulations; (c) upconversion spectra resonant with dark excitons^[108], with the inset showing a schematic of the phonon-assisted upconversion process; (d) relationship between upconversion enhancement factor and dark exciton excitation^[108], with the gray shaded area indicating low dark exciton excitation and the orange shaded area indicating high dark exciton excitation; (e) comparison of enhancement effects between cubic and nanosphere microcavities^[108]; (f) schematic of the cubic microcavity structure^[108]; (g) schematic of the gold nanorod microcavity structure^[39]; (h) schematic of the dual-resonant microcavity enhancement principle^[39]; (i) schematic of the dual-resonant microcavity structure^[39]; (j) power dependence of the upconverted emission spectra, with the inset showing the spatial distribution of the enhanced upconversion in the microcavity^[39]; (k) power dependence of the upconversion enhancement factor (top) and comparison between enhanced and unenhanced upconversion (bottom)^[39]

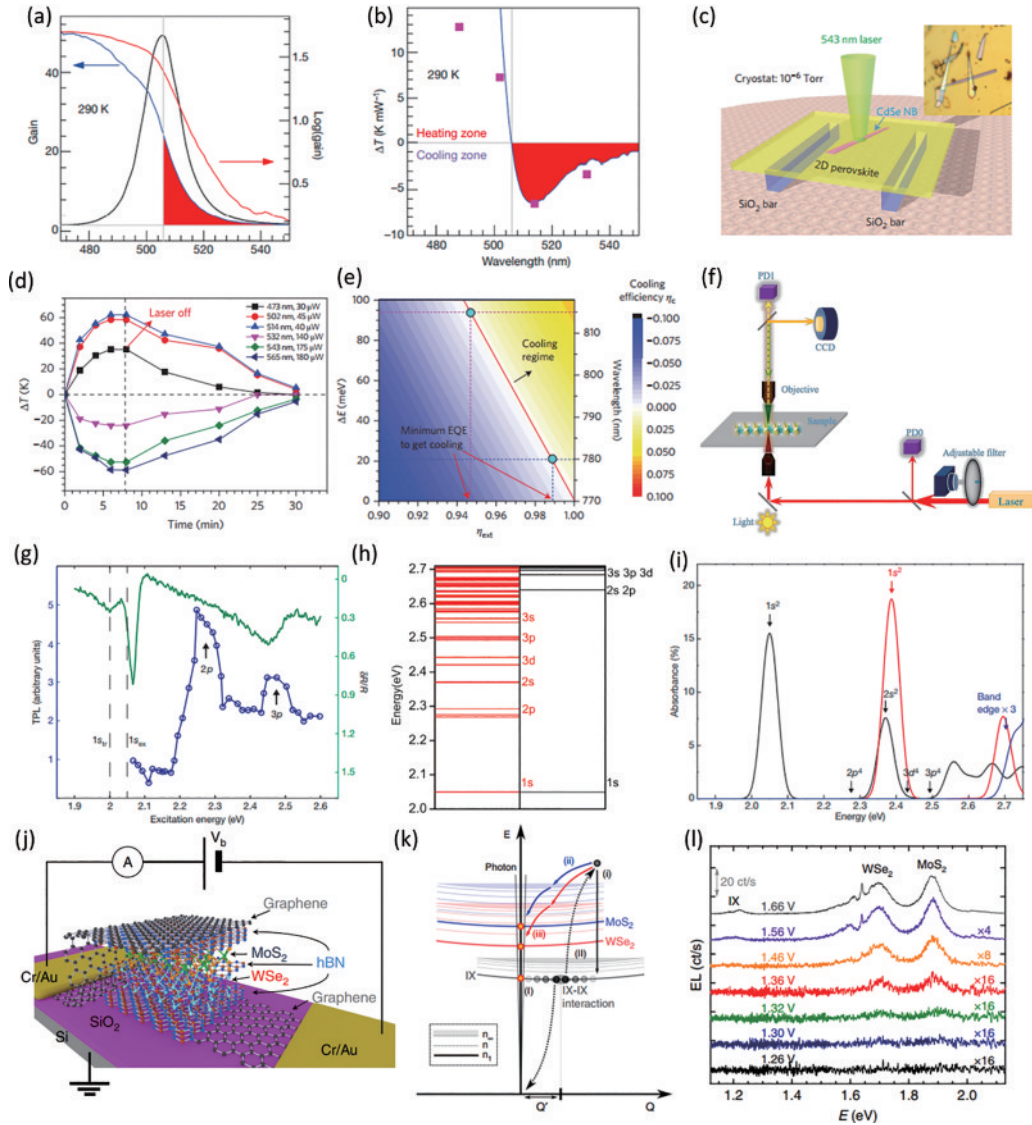


图 12 上转换发光的应用。(a) 上转换发光的光致发光谱(黑色曲线)和吸收谱(蓝色曲线),红色曲线为半指数坐标的吸收谱,红色区域为可以实现光学冷却的光谱范围^[5]; (b) 温度变化的波长依赖特性,红色区域为可以实现光学冷却的光谱范围^[5]; (c) 光学制冷装置示意图^[86]; (d) 不同波长下温度变化与时间的关系^[86]; (e) 外量子效率、上转换光子能量增益与光学制冷效率之间的关系^[86],红线右侧为可以实现制冷的区域; (f) 通过双光子上转换发光探测暗激子态的实验光路示意图^[112]; (g) 双光子上转换探测暗激子态,蓝色曲线为双光子上转换发光光谱,绿色线为线性吸收导致的反射率变化^[113]; (h) GW-BSE模型计算的激子能级(左图)和传统氢原子模型计算的激子能级(右图)^[113]; (i) GW-BSE模型计算的A(黑色)和B(红色)激子吸收谱^[113]; (j) WSe₂/MoS₂异质结电致发光器件结构示意图^[112]; (k) WSe₂/MoS₂异质结俄歇复合发光原理示意图^[112]; (l) WSe₂/MoS₂异质结电致发光光谱^[112]

Fig. 12 Applications of upconversion photoluminescence. (a) Photoluminescence spectrum (black curve) and absorption spectrum (blue curve) of upconversion photoluminescence, with the red curve showing the absorption spectrum in semi-log coordinates, and the red shaded region indicates the spectral range where optical cooling can be achieved^[5]; (b) wavelength dependence of the temperature change, with the red shaded region indicating the spectral range for optical cooling^[5]; (c) schematic of the optical refrigeration setup^[86]; (d) relationship between temperature change and time under different wavelengths^[86]; (e) relationships between external quantum efficiency, upconverted photon energy gain, and optical cooling efficiency, the region to the right of the red line can achieve cooling^[86]; (f) schematic of the experimental setup for probing dark exciton states via two-photon upconverted electroluminescence^[112]; (g) probing dark exciton states by two-photon upconversion photoluminescence, with the blue curve showing the upconversion spectrum and the green line showing the reflectivity change caused by linear absorption^[113]; (h) excitonic energy levels from GW-BSE calculations (left) and from a hydrogenic model (right)^[113]; (i) A (black) and B (red) exciton absorption spectra from GW-BSE calculations^[113]; (j) schematic diagram of the structure of the electroluminescence device based on a two-dimensional material heterojunction^[112]; (k) schematic diagram of the Auger recombination luminescence in the WSe₂/MoS₂ heterojunction^[112]; (l) electroluminescence spectrum of WSe₂/MoS₂ heterojunction^[112]

光光谱中无法体现的暗激子态进行探测^[112-113]。对于 WS₂ 单层,研究者通过双光子吸收上转换探测到了暗激子态^[113][图 12(g)],并验证了暗激子态与传统的氢原子模型不符[图 12(h)],验证了考虑量子限域效应的 GW-BSE 模型的正确性[图 12(i)]。

5.3 电致发光器件

除了用光激发产生上转换发光,也可以通过在二维材料上加偏置电压的方式产生上转换发光。Binder 等通过在 WSe₂/MoS₂ 异质结中注入电子的方式,在偏置电压远小于带隙对应的电压时观测到了上转换发光现象。器件结构如图 12(j)所示,研究者将石墨烯电极放在二维材料的顶端和底端并加入偏置电压,注入的电子和空穴形成层间激子[图 12(k)],随后一个层间激子非辐射复合的能量激发另一层间激子到 WSe₂ 和 MoS₂ 的导带之上,并通过俄歇复合的方式产生上转换发光现象。需要特别注意的是,研究者还在二维材料之间加入 hBN 层以抑制层间激子的辐射复合,从而增强上转换发光现象。实验结果如图 12(l)所示,研究者在偏置电压约为 1.3 V 时便观测到了光信号,这个偏置电压远小于 WSe₂ 和 MoS₂ 的带隙能量,因此证实发生了上转换发光现象。这种器件结构通过电致俄歇复合发光的方式观测到了层间激子与层间激子的相互作用,并为激子凝聚态和超流态的实现提供了新机遇。

6 结束语

二维材料优异的光学性质为上转换发光提供了一个新颖的平台,其独特的上转换发光机制引起了广泛的研究兴趣和探索,其高效率、可灵活调控的性能优势也在激光制冷、亚能带探测、电致发光器件等领域展现出潜在的应用价值。尽管如此,由于二维材料仅有原子层级别的厚度,其与光相互作用的距离极短,限制了上转换发光的量子效率,因此对发光效率的优化是亟待解决的问题。微腔增强和异质结增强等方式具备大幅提高上转换发光效率和强度的潜力,值得研究者进一步探索,此外转角堆叠对上转换发光的影响机制和在器件上的应用也值得进一步深入研究。在理论上,二维材料同时具备电子-电子和电子-声子相互作用,因此一个完备的光子-电子-声子相互作用模型将有助于进一步系统分析上转换发光的新机制,以及设计增强上转换发光的新结构。相信未来随着器件性能的改进和设计的不断完善与优化,二维材料上转换发光可以拓展出更加广泛的应用前景。

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