

基于相干电子源的超快低能电子全息成像

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摘要 在原子尺度上研究电荷输运超快动力学特性,对于揭示光催化、光合作用等物理化学过程的机制有着重要意义。与高能(>20 keV)电子束相比,低能(<500 eV)电子束在样品表面微弱的局域电场下较大的散射截面,结合全息成像机制,可以实现亚纳米级的空间分辨能力。因此,若采用具有飞秒时间分辨能力的超快相干电子源,低能电子全息成像有望实现对原子尺度的电荷输运超快动力学过程的表征。首先介绍了超快低能电子全息成像的原理,然后讨论了超快相干电子源的产生机制和性能,在此基础上,阐述了超快低能电子全息成像的研究现状并展望了未来的发展趋势。

关键词 全息; 电子全息成像; 低能电子成像; 超快电子源; 相干电子源; 场发射; 电荷输运超快动力学

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1 引言

研究原子尺度的电荷输运超快动力学过程,如载流子激发、光致电荷分离、电荷转移及能量转移等,对于推动光催化、光合作用、发光、光伏等领域的发展具有重要意义。超快电子显微镜是实现高时间-空间分辨动力学过程表征的必要手段。其中,超快透射电子显微镜(TEM)^[1-3]和超快扫描电子显微镜(SEM)^[1,4]已经可以实现纳米尺度乃至亚纳米尺度超快动力学过程的实空间观测,如原子扩散过程^[5]、化学反应过程^[6-8]、相变过程^[9]、生物大分子动力学^[10]等。超快TEM、超快SEM通常采用高能(>20 keV)电子束进行成像,然而,高能电子束散射截面较小,导致其对样品局域微弱电场或光场的检测灵敏度低,难以表征瞬态电荷输运过程^[11]。相比之下,低能电子显微镜利用能量小于500 eV的电子进行全息成像,高能电子束在样品微弱的局域电场和纳米结构表面瞬态光场下的散射截面和散射偏转角较大^[11-13];同时,其空间分辨率也可达 10^{-10} m量级^[14]。因此,低能电子全息成像^[11,15-16]对电荷输运过程具有更高的探测灵敏度,与超快激光时间分辨技术结合时,有望实现原子级的局域电磁场分布及电荷输运动力学表征^[11,13,17-18]。

点电子源投影(简称“点投影”)显微镜是实现低能电子全息成像最简单的装置^[11,19]。由于无须匹配复杂

的电子光学系统,因此没有像差,其极限空间分辨率主要取决于电子源的相干性^[20],包含横向相干性和纵向相干性。其中,前者取决于电子源的虚源半径,后者取决于电子源的能量散度(简称能散)。据报道,使用原子级单晶钨针尖电子源可以实现对单个蛋白质分子^[21]、单个DNA分子^[22]、石墨烯晶格^[14,23]以及亚纳米尺度荷电状态^[24]等的静态全息成像。同时,采用超快电子源^[17,25-28],可获得亚10 fs的时间分辨率,并实现对电荷转移超快动力学过程的表征^[13,18,29]。然而,飞秒激光引起的热效应^[30-31]、光子能量失配^[32-35]和强光场加速^[36]等都会削弱电子源的相干性,因此基于金属针尖的电子全息成像空间分辨率仅能达到数纳米^[37-38]。故获取更高相干性的超快电子源是实现原子级空间分辨的超快低能电子全息成像的关键。

本文首先对低能电子全息成像的原理进行介绍,然后对超快相干电子源的产生机理及发射电子的相干性进行阐述,随后结合超快低能电子全息成像的研究现状,阐明了相干电子源对提高空间分辨率的重要性,最后对利用超快相干电子源提高超快电子全息成像的空间分辨率进行展望。

2 超快低能电子全息成像的基本原理

低能电子全息成像^[15-16]的原理如图1所示。整个

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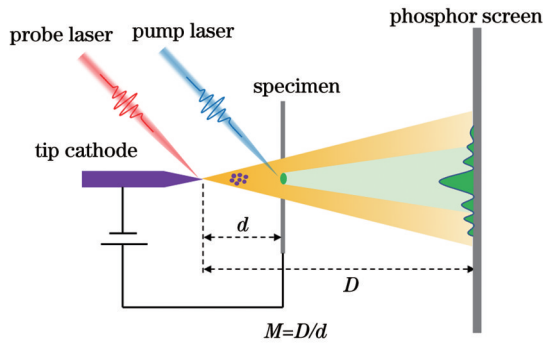


图1 超快电子全息成像原理图

Fig. 1 Schematic of ultrafast electron holography

装置主要包含三个部分：针尖点电子源、样品和荧光屏。针尖与样品之间的距离为 d ，针尖与荧光屏之间的距离为 D ，其成像放大倍数 $M = \frac{D}{d}$ 。当电子源具有足够高的相干性且针尖与样品之间的距离足够小时，电子的投影像不仅包含样品形貌引起的衬度变化，还包含了透过样品的电子束与未经过透射样品的电子束（参考电子束）叠加后形成的干涉条纹，即形成了全息像^[11,15]。通过对全息像进行重构^[39-40]，即可得到原子级分辨的样品形貌像^[11,23,41]。

电子全息成像的极限分辨率(g)主要取决于电子源相干性。电子源相干性主要分为横向相干性（也称为空间相干性）和纵向相干性（也称为时间相干性）。横向相干性用横向相干长度(ξ)来衡量，指在电子束辐照的空间中任意两点发生相干的最大距离，可通过测量干涉条纹区域的宽度得到^[38]。 ξ 取决于电子源的虚源半径 r ，二者之间的关系是 $r = \frac{\lambda D}{\pi \xi}$ ^[38,42]，其中 λ 是电子束波长。又因 $g \approx 2r$ ^[43]，可见，电子源的虚源半径越小，横向相干性则越高，空间分辨能力则越强。虚源半径与针尖曲率半径、场增强因子以及材料功函数相关。

具体地说，针尖的曲率半径越小、场增强因子越大及功函数越大，则虚源半径越小。同时，干涉条纹的数量和宽度亦会受纵向相干长度 L 的影响。若纵向相干性较差，电子全息像中干涉条纹的数量会减小。 L 可由电子飞行速度 v 和时间 t 相乘得到，即 $L = v \cdot t$ ^[43]，其中飞行速度 $v = \sqrt{\frac{2E}{m}}$ ，飞行时间 $t = \frac{h}{2\pi\Delta E}$ ， E 为电子能量， m 为电子质量， ΔE 为电子能散， h 为普朗克常量。可见，电子能散 ΔE 越小，纵向相干性则越高，则越有利于提高空间分辨率。

在上述电子全息成像装置的基础上，引入飞秒激光泵浦探测技术，可以实现超快动力学表征^[3,7-8]，其原理如图1所示。泵浦激光用来激发样品的超快过程，探测激光用来激发电子发射，形成探测电子束。其时间分辨能力取决于电子束的脉宽，脉宽越小，则时间分辨能力越高。值得注意的是，电子从针尖到样品的传输路径较短，可极大地避免电子束长程传输过程中的脉宽展宽，因此，更容易实现高时间分辨率^[17,37]。

综上所述，发展具有高时空相干性和窄脉宽（飞秒-阿秒）的电子源，是实现原子尺度超快电子全息成像技术的关键。

3 超快相干电子源产生机制及发射电子的相干性

场发射(FE)是指在强电场条件下阴极材料释放电子的过程，虚源半径可达亚纳米尺度，能散可达1 eV以下。相比于其他发射机制^[44]，场发射是构筑相干电子源的最优选择。通过使用脉冲激光激发阴极的光电子发射，可获得超快电子源。光电子发射机制包括：光子辅助场发射(PFE)、多光子光电子发射(MPP)、阈上光电子发射(ATP)以及光场电子发射(OFE)，如图2(a)~(d)所示^[25,36]。

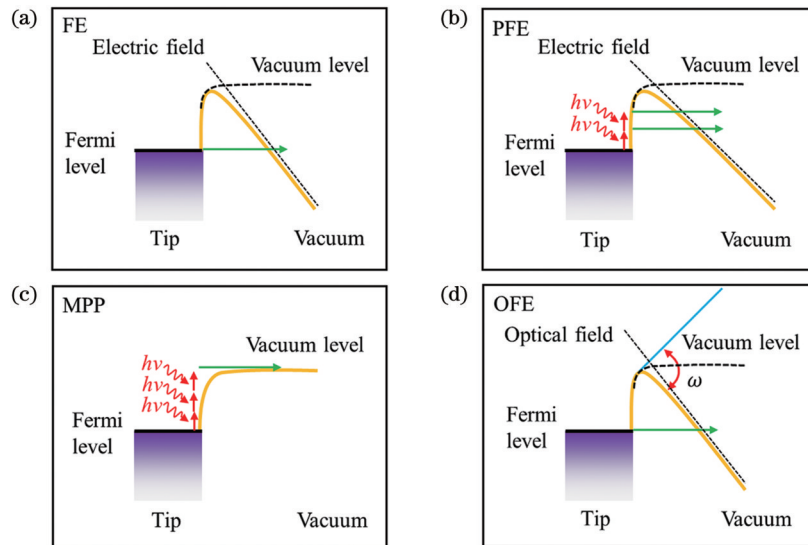


图2 不同的光电发射机制示意图^[25,36]。(a)FE;(b)PFE;(c)MPP;(d)OFE

Fig. 2 Schematics of different photoemission mechanisms^[25,36]. (a) FE; (b) PFE; (c) MPP; (d) OFE

3.1 FE的基本原理及电子的相干性

场发射的原理:利用外加强电场压缩发射材料表面的真空势垒,形成电子隧穿发射,如图2(a)所示。场发射现象是Fowler和Nordheim在1928年发现的。发射

电流强度可以由公式 $J = \frac{c_1(\beta E)^2}{\Phi} \exp\left(-\frac{c_2\Phi^3}{\beta E}\right)$ 决定^[45],其中 J 是发射电流密度, β 是局域场增强因子, E 是电场强度, Φ 是材料功函数, $c_1 = \frac{e^3}{8\pi h}$, $c_2 = \frac{8\pi\sqrt{2m}}{3eh}$, e 是电子电荷量。一方面, J 和 β 呈指数关系,且电子主要由发射尖端的原子级凸起结构发射,因此,场发射电子源具有较小的虚源半径。另一方面,由于隧穿电子来自费米能级附近,因此可以实现较低的能散。

例如,单原子钨针尖发射源的虚源半径可以低至 0.14 nm ^[46],能量散度最低可达 0.2 eV ^[38]。

3.2 PFE、MPP、ATP和OFE的基本原理及发射电子的相干性

PFE原理如图2(b)所示,电子在吸收一个或者多个光子的能量之后被激发到高能级,然后在外加静电场的作用下隧穿到真空中。如果提高激光功率,发射模式可从单光子PFE模式转变为多光子PFE。同一电子吸收的光子个数等于光电流-光功率幂指数(n),如图3(a)所示^[32]。若电子吸收足够多的光子,使其能量大于发射阈值,则即使没有静电场的存在,电子亦可发射到真空中,该过程为MPP,如图2(c)和3(b)所示。其中PFE产生的能谱峰与静态场发射峰的峰宽相近,所发射的电子能散较小;而MPP发射峰则较宽,所发射的电子能散较大,如图3(c)、(d)所示^[47]。

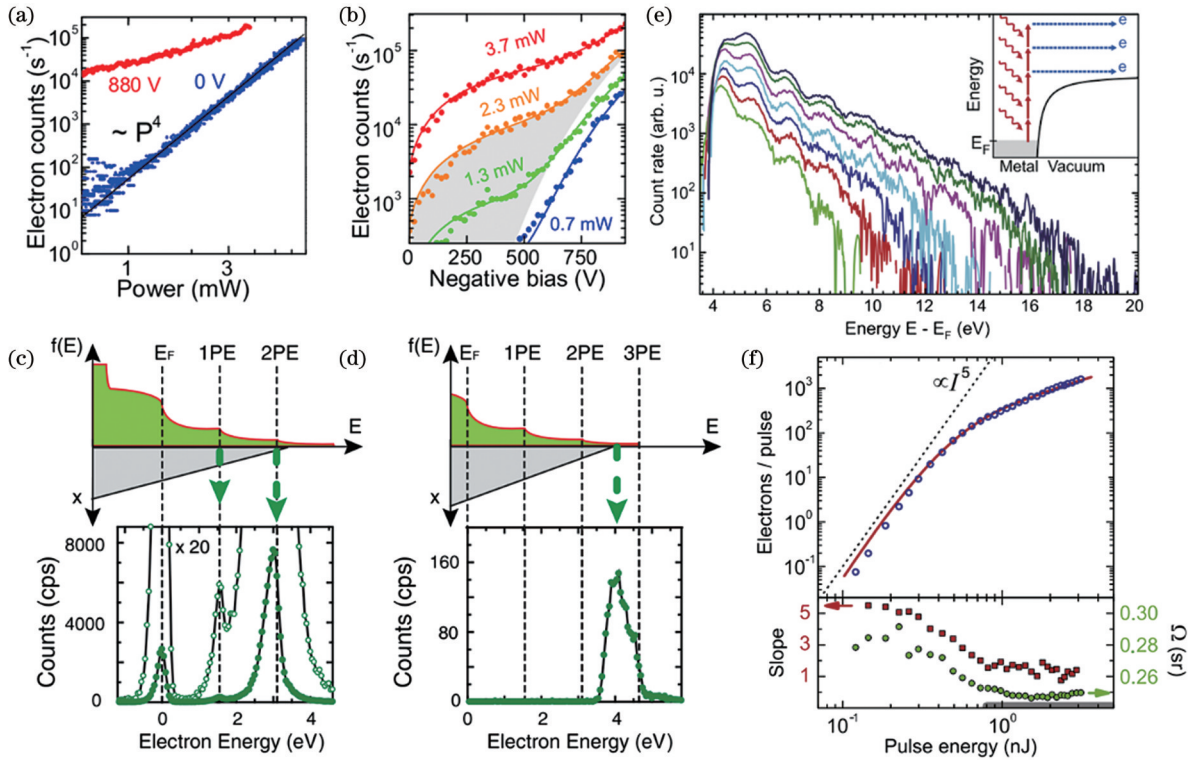


图3 PFE、MPP和ATP机制。(a)曲率半径为20 nm的金针尖在激光照射下的光电子发射与功率之间的关系,其中偏置电压880 V对应PFE过程,偏置电压0 V对应MPP过程^[32]; (b)不同光功率下的光电子发射率与偏压之间的关系^[32]; (c)PFE光电子能谱^[47]; (d)MPP光电子能谱^[47]; (e)ATP光电子能谱^[33]; (f)光电子发射率-光强曲线^[36]

Fig. 3 Mechanisms of PFE, MPP and ATP. (a) Relationship between photoelectron emission and power of gold tip with curvature radius of 20 nm under laser irradiation where bias voltage of 880 V corresponds to PFE process and bias voltage of 0 V corresponds to MPP process^[32]; (b) relationship between photoelectron emissivity and bias at different optical powers^[32]; (c) PFE photoelectron spectroscopy^[47]; (d) MPP photoelectron spectroscopy^[47]; (e) ATP photoelectron spectroscopy^[33]; (f) photoelectron emissivity-light intensity curve^[36]

若继续增加激光的功率,则会有更多的光子参与到电子激发过程中(光子数目比功函数所需光子数目多),该过程称为ATP,如图3(e)中插图所示。ATP光电子能谱会有更多的峰出现,每个峰对应一个光子能量,如图3(e)所示^[33]。在ATP模式下,光电子能散较大。

随着光强的进一步增加,光电子发射进入OFE模

式^[36],其原理如图2(d)所示。在OFE模式下,发射电流-光功率曲线会出现“弯曲”,幂指数随着光功率的增

加而减小,如图3(f)所示。用Keldysh参数 $\gamma = \sqrt{\frac{\Phi}{2U_p}}$ 可以描述这一发射行为,其中有质动力势 $U_p = \frac{e^2 F_{\text{eff}}^2}{4m\omega^2}$,

ω 为光的频率, F_{eff} 为针尖尖端的有效电场强度^[25,48]。当 $\gamma \gg 1$ 时, 光电子发射机制为 MPP; 当 $\gamma \ll 1$ 时, 光电子发射模式为纯净的 OFE; 而当 $\gamma \approx 1$ 时, 光电子发射机制为 MPP 和 OFE 的混合机制^[25]。

当光电子发射完全进入到 OFE 模式时, 光电子能谱会出现“平台”现象。“平台”特征主要是电子在光场中发生再散射所致, 且能谱截止能量约为 $10U_p$ 。Krüger 等^[49] 通过使用超短脉冲激光激励钨针尖, 实现了 OFE [图 4(a)], 并观察到了光电子发射能谱 [图 4(b)] 中的“平台”特征, 截止能量可达 ~ 13 eV。

OFE 模式的另一个显著特征是, 光电子发射会受到激光脉冲载波包络相位 (CEP) 的调制, 如图 4(b) 所示。此外, 当激光波长增加或者针尖曲率半径减小时, 电子在光场中的运动模式会由“颤动”转变为“亚周期”, 即电子不再随着交变光场的变化发生往复运动, 而是在光场中经历了半个光波周期的加速后飞离光场, 如图 4(c) 所示^[48]。此时, 光电子能谱的截止能量小于 $10U_p$, 且随着激光频率的减小, 截止能量保持不变, 如图 4(d) 所示^[48]。

利用 OFE 模式可以获得亚光学周期分辨的光电

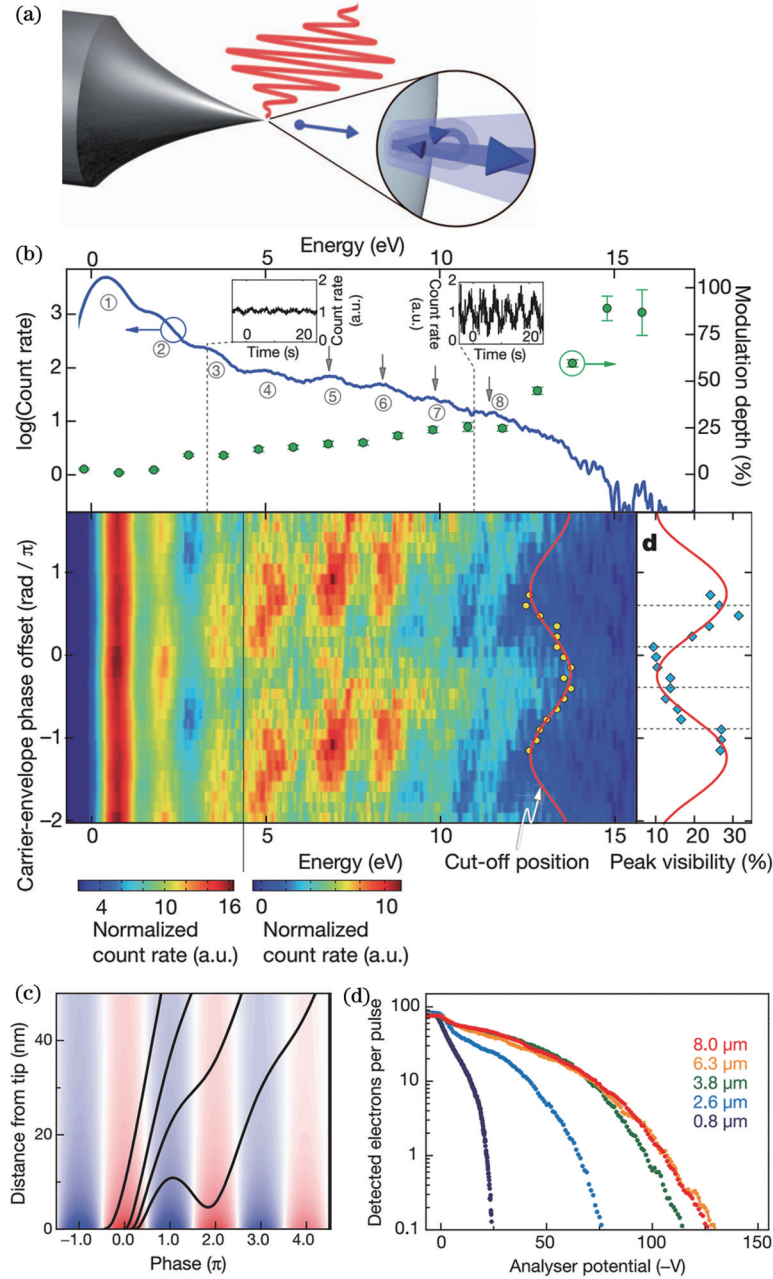


图4 OFE机制。(a)OFE示意图^[49]; (b)OFE能谱及光电流的CEP依赖关系^[49]; (c)具有不同初始发射相位的电子的飞行轨迹仿真, 激光中心波长为8 μm ^[48]; (d)不同激光波长下的光电子发射率与分析电压之间的关系^[48]

Fig. 4 Mechanism of OFE. (a) Schematic of OFE^[49]; (b) OFE energy spectrum and CEP dependence of photocurrent^[49]; (c) simulated flight trajectories of electrons with different initial emission phases and laser center wavelength of 8 μm ^[48]; (d) relationship between photoelectron emissivity and analyzer potential at different laser wavelengths^[48]

子发射,其电子束脉宽可达亚飞秒量级。然而,“颤动”模式不仅使光电子能谱展宽,还使电子发射的初始方向发生改变,并引起针尖虚源半径的增加,进而导致发射电子的相干性变差。而“亚周期”模式有效避免了电子的不均匀加速,可以实现更小的能散和虚源半径,电子具有更高的相干性。

表 1 对比了不同光电子发射机制下电子的相干性。其中,PFE 机制下电子具有更高的相干性,原则上

可以通过该机制实现飞秒量级的原子分辨超快电子源。然而,由于金属针尖本身具有连续能级,其电子服从费米-狄拉克分布,因此其相干性还受到激光热效应的影响^[30-31]。此外,为了进一步提高时间分辨率,必须采用 OFE 机制,但同时降低其发射能散,这样才能实现原子级分辨。金属针尖由于物性限制,很难进一步降低能散,无法同时实现亚飞秒和原子级分辨。综上所述,发展新型超快相干电子源材料势在必行。

表 1 不同光电子发射机制下的电子相干性

Table 1 Electron coherence under different photoelectron emission mechanisms

Photoemission mechanism	Electron pulse width	Electron energy spread	Virtual source size	Coherence
PFE	fs	Small	Small	Largest
MPP	fs	Large	Large	Larger
ATP	fs	Larger	Larger	Large
OFE	sub-fs	Largest	Largest	Small

3.3 低维材料超快电子源及其相干性

与金属针尖相比,低维电子发射材料具有显著优势。第一,原子级的发射位点更容易提供原子级的虚源半径,实现横向相干^[46]。第二,离散能带结构可以有效避免费米-狄拉克分布的热展宽,从而降低电子发射能散,实现纵向相干^[50]。此外,其丰富的电子结构可调整维度是电子源性能优化的重要基础。

例如,Li 等^[51]利用单壁碳纳米管(简称碳管)尖端半径小的优势,实现了空间光场的充分压缩,从而抑制了电子的“颤动”效应,进而实现了高准直电子发射,并获得了 0.25 eV 的超低能量散度[图 5(a)、(b)],比金属低一个数量级^[50]。同时,Li 等^[52]还提出一种价带电子强光场发射理论模型[图 5(c)]:一维碳管具有离散的能带结构,在光场较弱的情况下,导

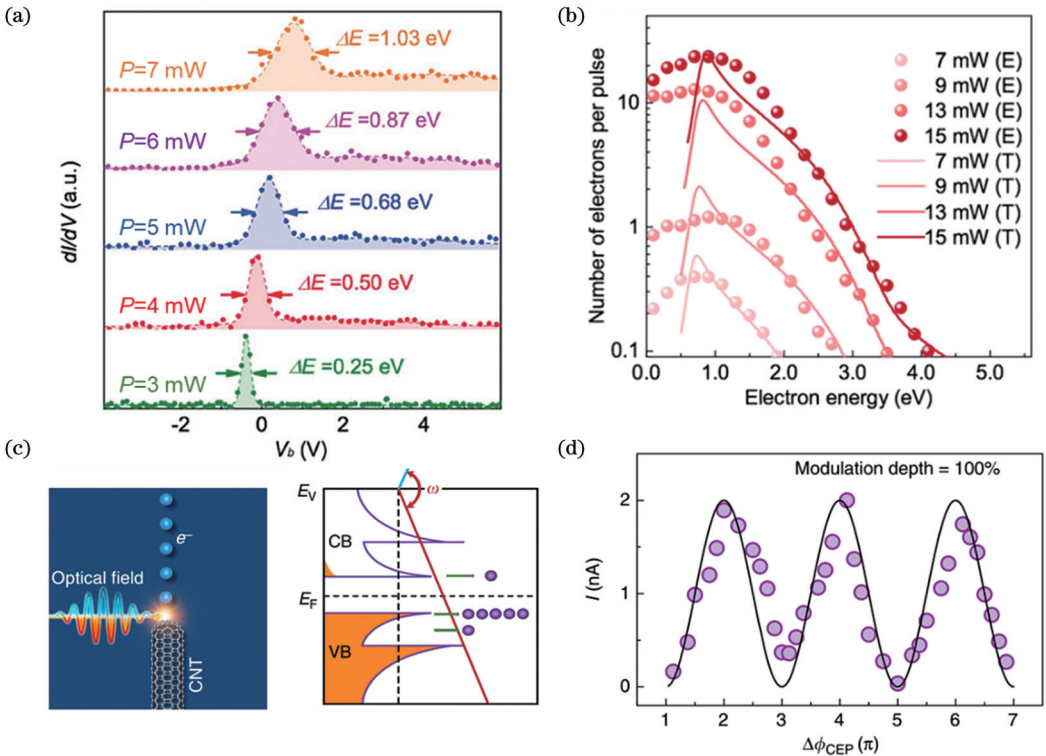


图 5 一维碳管 OFE。(a)碳管光场发射的微分电导曲线^[50];(b)碳管光场发射的光电子能谱^[51];(c)碳管光场发射示意图和价带发射示意图^[52];(d)OFE 光电流的 CEP 依赖关系^[52]

Fig. 5 OFE of one dimensional carbon tube. (a) Differential conductance curves of OFE through carbon tube^[50]; (b) photoelectron spectra of OFE through carbon tube^[51]; (c) schematics of OFE through carbon tube and valence band^[52]; (d) CEP dependence of OFE current^[52]

带电子发射占主导,随着光场的增强,价带电子开始发射并占主导。在从导带发射向价带发射转变的过程中,会出现一个极端非线性的发射行为,使得脉冲激光的 CEP 对光电发射的调制深度高达 100%,如图 5(d)所示^[52]。以上工作证明,碳管超快电子源同时具备单色性好、准直度高和光学相位调制精度高三个优点,可以满足原子尺度时空分辨成像对电子源的要求。

此外,Purcell 等^[53]通过在 Pt 纳米尖端构筑零维量子结构,实现了分立能级的共振隧穿场发射。共振隧穿效应与激光法布里-珀罗腔谐振类似,具有极好

的能量选择特性,使得发射电子的能散低至 64 meV,远小于钨针尖的 0.2 eV。Esat 等^[54]在 Ag(111)单晶表面构筑了基于单分子的电子发射体,实现了单一能级的场发射,并观测到了单分子尺度的电子束干涉条纹,因此,单分子电子源展现出了极好的相干性[图 6(a)~(c)]。以此为理论基础,Duchet 等^[55]通过在钨针尖尖端修饰量子点,构筑了双势垒隧穿结构,初步实现了 PFE 效应主导的共振隧穿场发射,其电子能散小于 0.5 eV[图 6(d)~(g)]。上述工作也为超快相干电子源的构建提供了新思路。

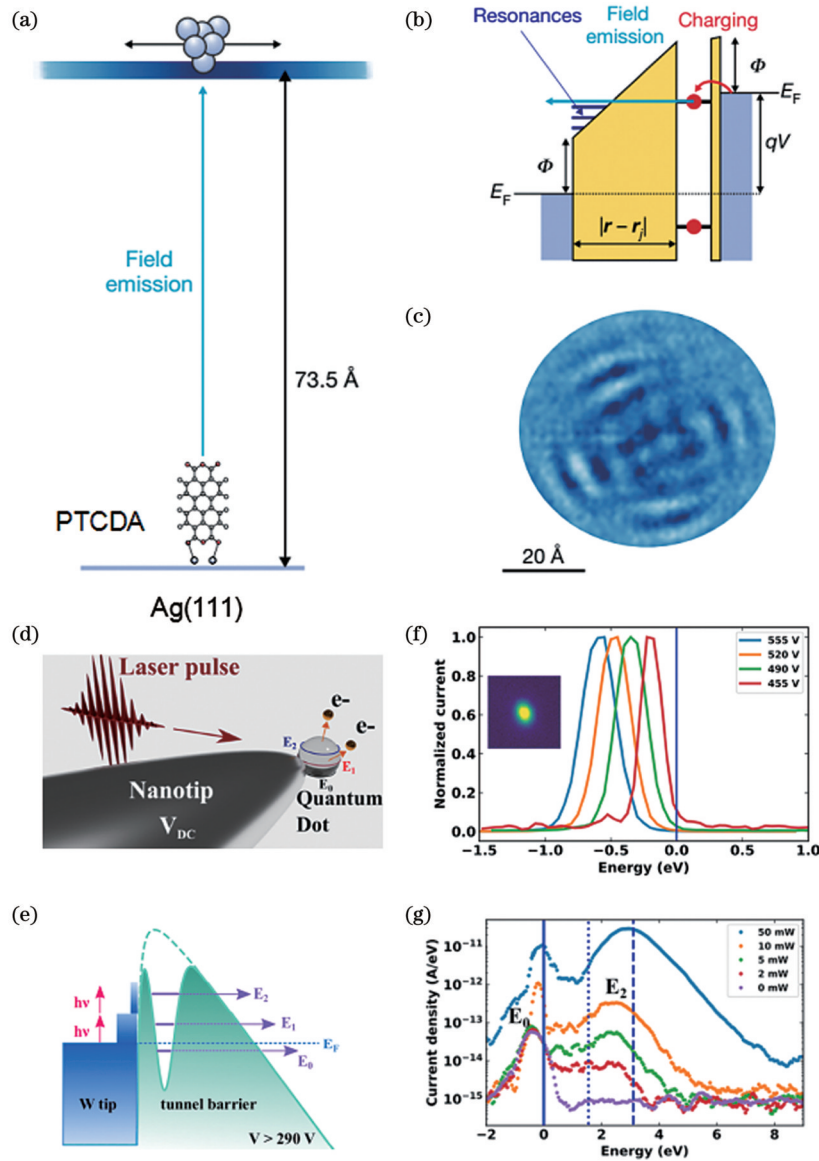


图6 基于零维纳米结构的场发射和光电子发射。(a)单晶银(111)基底上的花四甲酸酐(PTCDA)分子场发射^[54]; (b)基于 PTCDA 分子的双势垒隧穿结构^[54]; (c)PTCDA 分子场发射的干涉成像^[54]; (d)钨针尖尖端修饰量子点示意图^[55]; (e)基于量子点的双势垒隧穿模型^[55]; (f)量子点静态场发射能谱^[55]; (g)量子点光电子发射能谱^[55]

Fig. 6 Field emission and photoemission based on zero-dimension nanostructure. (a) Field emission of perylene-3,4,9,10-tetracarboxylic acid dianhydride (PTCDA) molecule deposited on Ag(111) substrate^[54]; (b) double barrier tunneling structure based on PTCDA molecule^[54]; (c) interference pattern of PTCDA molecule FE^[54]; (d) illustration of quantum dot modified by apex of tungsten tip^[55]; (e) double barrier tunneling model based on quantum dot^[55]; (f) static field emission spectra of quantum dots^[55]; (g) quantum dot photoelectron emission spectra^[55]

表 2 汇总了影响发射电子相干性的因素。不难看出,为了获得极限时空分辨的电子源,不仅需要在选择合适电子发射机制的基础上优化激光和环境参量,还需要优化设计发射材料。其中,以碳管为代表的低维材料超快相干电子源是必然发展趋势。

表 2 各种因素对发射电子相干性的影响
Table 2 Influence of different factors on electron coherence

Factor	Electron energy spread	Virtual source size	Coherence
Laser power	Positive correlation	Positive correlation	Negative correlation
Laser wavelength	Positive correlation	Positive correlation	Negative correlation
Radius of curvature	Positive correlation	Positive correlation	Negative correlation
Quantized level	Negative correlation		Positive correlation
Thermal effect	Positive correlation		Negative correlation

4 超快低能电子全息成像的研究现状

4.1 静态低能电子全息成像的研究现状

1948 年 Gabor^[16]就已经预测了电子全息成像可实现原子尺度空间分辨表征,然而,由于受到原子级高相干电子源制造技术和扫描探针控制技术的限制,该预测并没有在实验上实现。直到 20 世纪 90 年代,随着相关技术的发展,基于点投影显微镜的低能电子全息成像得以实现^[15],且研究者完成了对石墨烯原子晶格以及单个生物大分子的高分辨表征。

例如,Longchamp 等^[14]基于单晶钨(111)针尖电子源,在针尖-样品距离约为 380 nm 的情况下,采用 58 eV 的低能电子,获得了单层石墨烯的原子分辨图像,如图 7(a)所示。Longchamp 等^[21]随后又将蛋白质分子沉积到单层石墨烯衬底上,进行了低能电子全息成像。在实验中,针尖-分子样品距离约为 100 nm,电子的能量为 60~140 eV,获得了单个蛋白质分子的全息图,并在重构之后得到了单个蛋白质分子的形貌图,分辨率为 0.7~0.8 nm,如图 7(b)所示。Fink 等^[22]利用能量为 70 eV 的电子,测得了单根 DNA 分子

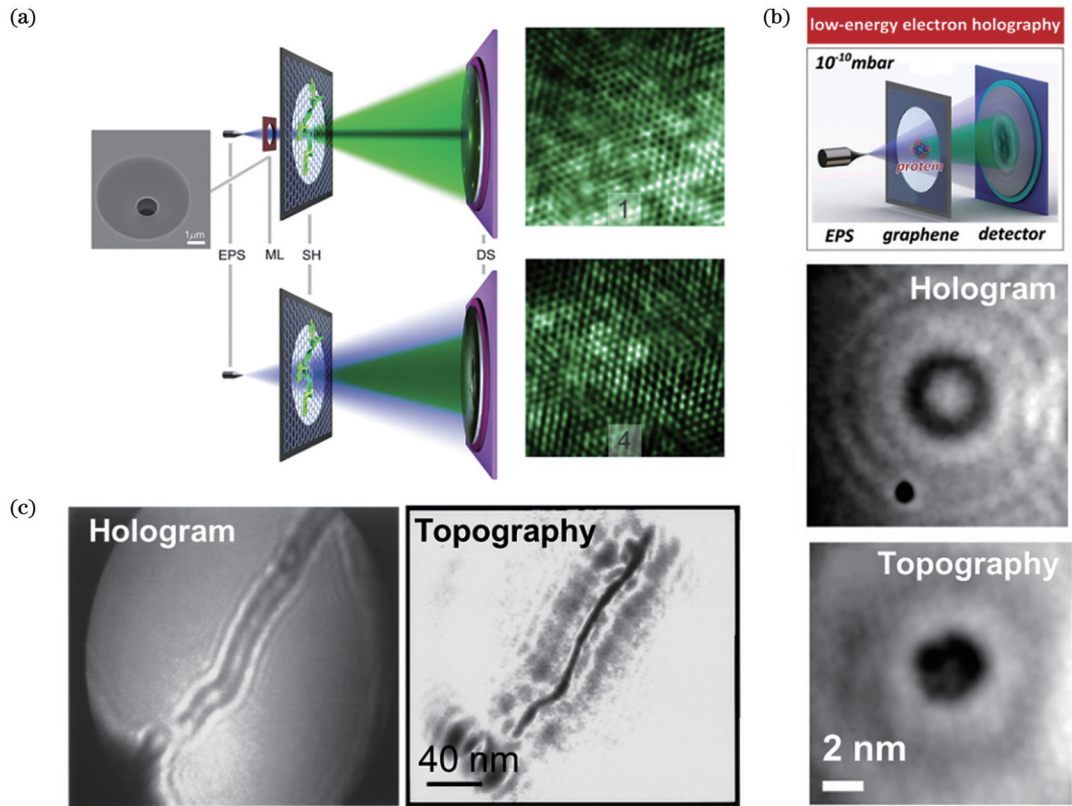


图 7 低能电子全息成像。(a)低能电子全息成像原理图及全息像重构之后得到的石墨烯形貌图和放大图^[14]; (b)DNA 分子的全息成像和重构之后的形貌图^[21]; (c)蛋白质分子全息成像及重构之后的形貌图^[22]

Fig. 7 Low energy electron holography. (a) Schematic of low-energy electron holography and graphene topography and detailed topography reconstructed from hologram^[14]; (b) DNA molecular hologram and its reconstructed topography^[21]; (c) protein molecular hologram and its reconstructed topography^[22]

的电子全息成像,并通过重构得到了DNA分子形貌图,如图7(c)所示。

具有小虚源半径和低能散的相干电子源是实现高空间分辨电子全息的基础。上述高分辨全息成像均依赖于高相干的原子级单晶钨针尖电子源,其尖端仅有一个或三个原子发射电子^[56],虚源半径极小,仅0.14 nm^[46],且能散低至0.2 eV。由于基于单色电子源的电子全息成像分辨率等于2倍的虚源半径,因此,单晶钨电子源可以使得电子全息成像获得近单原子级的空间分辨能力。电子全息的空间分辨能力可以与TEM和SEM

相媲美。

4.2 超快低能电子点投影成像及电荷输运超快动力学过程研究

将超快激光时间分辨技术与电子全息成像相结合,有望实现原子级空间分辨和飞秒时间分辨的超快动力学表征。然而,引入的超快激光必然会引起电子源相干性的恶化,超快电子全息成像的实验难度远高于静态电子全息成像。当电子源相干性无法满足全息成像要求时,只能进行单纯的点投影放大成像[图8(a)]。即使如此,由于电子源与样品之间的距

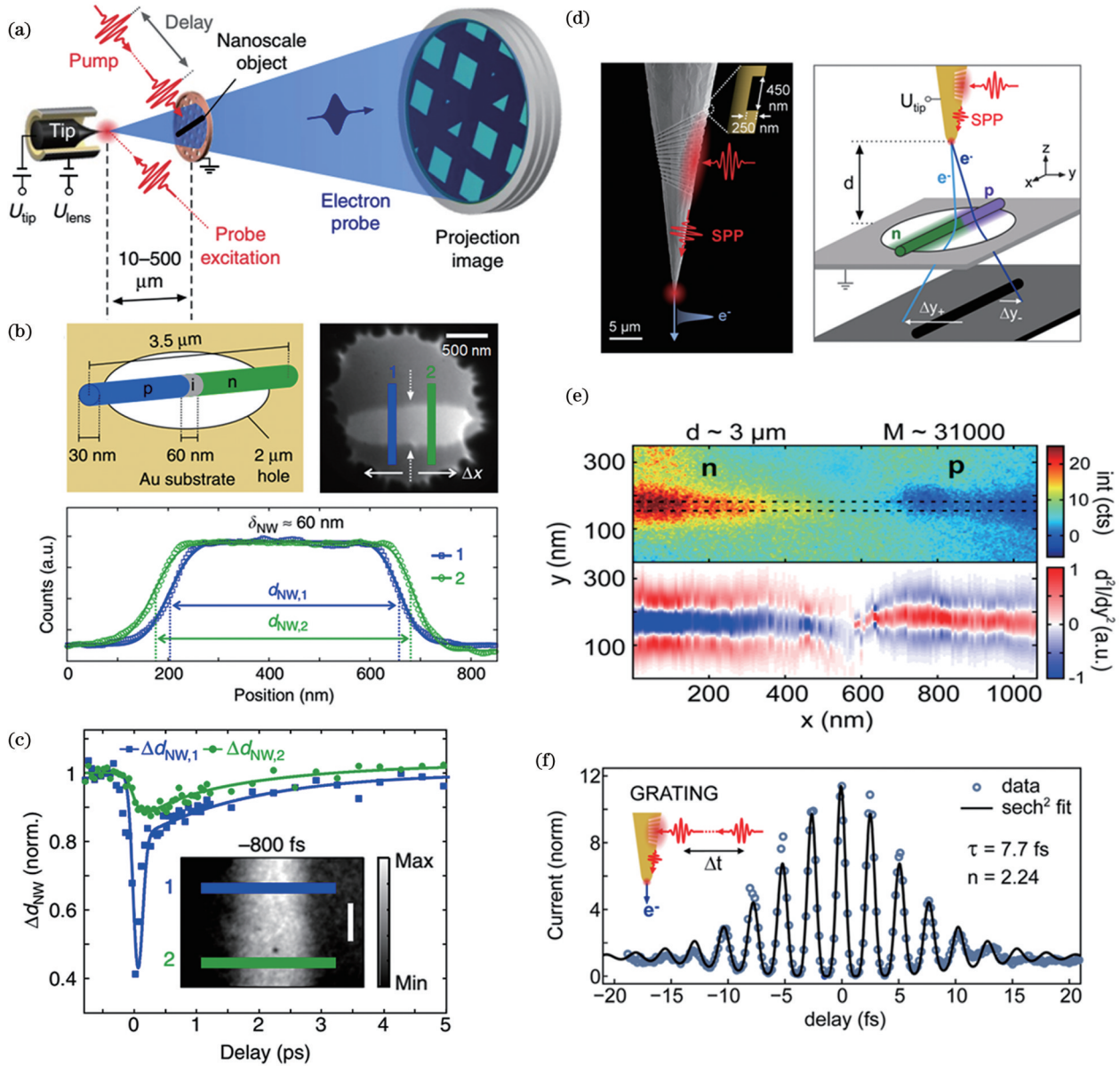


图8 超快低能电子点投影成像及电荷输运超快动力学过程研究。(a)超快低能电子点投影成像原理图^[18]; (b)p-i-n InP 纳米线结构示意图和点投影形貌图^[18]; (c)p-i-n InP 纳米线体内载流子瞬态响应曲线^[18]; (d)基于光栅结构的传播等离激元聚焦原理图和InP 纳米线点投影成像原理图^[17]; (e)InP 纳米线点投影形貌图^[17]; (f)基于光电流的激光自相关干涉测试^[17]

Fig. 8 Ultrafast low-energy electron point projection imaging and its application in ultrafast charge transport characterization. (a) Schematic of ultrafast low-energy electron point projection imaging^[18]; (b) schematics of p-i-n InP nanowire structure and point projection imaging^[18]; (c) carrier transient response curve in p-i-n InP nanowires^[18]; (d) schematic of laser focusing through propagating plasma focusing based on grating structure and schematic of InP nanowire point projection imaging^[17]; (e) InP nanowire point projection topography^[17]; (f) photocurrent-based laser autocorrelation interference measurement^[17]

离超短,因此超快电子全息成像可以有效避免电子长程传输过程中的脉宽展宽,在时间分辨率方面相比超快 TEM 更具优势,所以同样引起了研究人员的关注。

例如,Müller等^[18]将脉冲激光引入到低能电子成像系统中[图8(a)],以曲率半径为20~100 nm的钨针尖作阴极,针尖与样品之间的距离控制在20 μm ,电子能量设置为90 eV,获得了放大近5000倍的点投影成像。最终,实现了数十纳米分辨的p-i-n InP纳米线形貌测量[图8(b)],并测得了纳米线内部激光脉冲诱导的持续近100 fs的电流瞬态变化,如图8(c)所示。通过在金纳米针尖远离尖端的位置构筑光栅结构,可以将泵浦激光和探测激光分离,避免两束光之间的串扰,如图8(d)所示。这样就可以把针尖和样品的距离控制到3 μm 以下,进而将放大倍数提高

到31000,并成功实现了PN结附近电场分布的检测,如图8(e)所示^[17]。同时,其时间分辨率可达10 fs[图8(f)],远优于超快 TEM 数百飞秒的时间分辨能力^[57]。以此为基础,Vogelsang等^[29]使用带有光栅结构且曲率半径小于20 nm的金针尖作电子源,设置针尖-样品距离约为2.7 μm ,电子能量为60 eV,实现了20 nm空间分辨的双孔纳米天线形貌表征,测得了持续25 fs的激光诱导的电荷转移过程,如图9(a)所示。Hergert等^[13]则依托类似装置实现了低能电子与局域电磁场相互作用的动力学过程的实空间直接观测,如图9(b)、(c)所示。以上实验报道表明,低能电子对微弱的局域电场和纳米结构表面的瞬态光场具有出色的探测能力。相关研究结果对电荷集体激发乃至束缚态能级的光激发研究均具有重要意义^[12,17]。

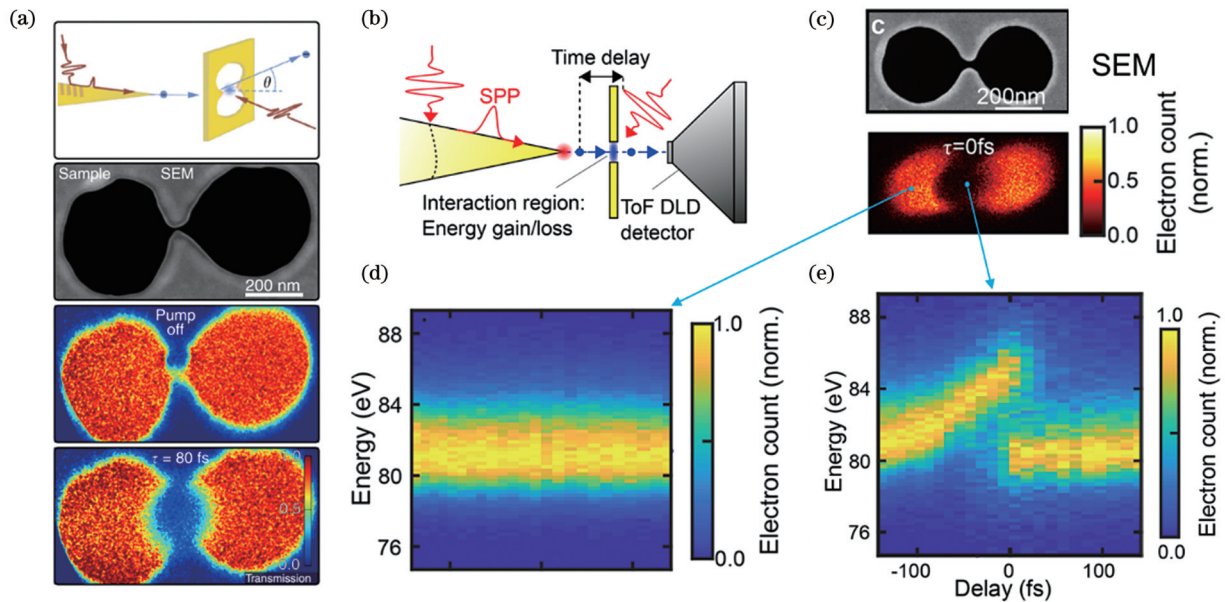


图9 超快低能电子点投影成像在电荷转移超快动力学研究中的应用。(a)双孔纳米天线结构的超快点投影成像^[29]; (b)纳米天线结构中电子能量分布的超快表征原理图^[13]; (c)0延时的纳米天线点投影成像^[13]; (d)纳米天线左侧区域的电子能量瞬态变化^[13]; (e)纳米天线中间区域的电子能量瞬态变化^[13]

Fig. 9 Application of ultrafast low-energy electron point projection imaging in study of ultrafast charge transport dynamics. (a) Ultrafast point projection imaging of double-hole nanoantenna structure^[29]; (b) schematic of ultrafast characterization of electron energy distribution in nanoantenna structure^[13]; (c) point projection imaging of nanoantenna at zero pulse delay^[13]; (d) transient variation of electron energy at left area of nanoantenna^[13]; (e) transient variation of electron energy at middle area of nanoantenna^[13]

4.3 超快低能电子全息成像

近年来,随着超快电子源研究的不断深入,单色性和虚源半径不断得到优化,因此超快低能电子全息成像得以成功实现。

例如,Ehberger等^[38]使用单晶钨相干电子源,对多壁碳管的超快电子全息成像进行了探索,如图10所示。其核心技术如下:调控外加电场,使得入射飞秒激光的光子能量与钨针尖的有效功函数相匹配,从而实现了低能散(0.51 eV)超快电子发射。因此,在针尖曲率半径约为10 nm、碳管样品到钨针尖距离小于1 μm 以及电子能量为41 eV的情况下,成功获得了多壁碳

管的超快电子全息图像,如图10(b)所示。根据虚源半径和相干长度的关系计算得,有激光辐照时电子源的虚源半径为 $(0.8 \pm 0.05) \text{ nm}$,可获得的极限空间分辨率为 $(1.6 \pm 0.1) \text{ nm}$ 。

在此之后,Vogelsang等^[37]通过使用中心波长为1.8 μm 和2.2 μm 的激光分别激发单晶金针尖(半径为9 nm)和单晶钨针尖(半径为6 nm),进行了超快低能电子全息成像。他们在两种针尖表面构筑了光栅结构进行激光聚焦[图10(c)],以减小针尖-样品距离。由于激光波长较长,单个光子能量低于功函数,因此

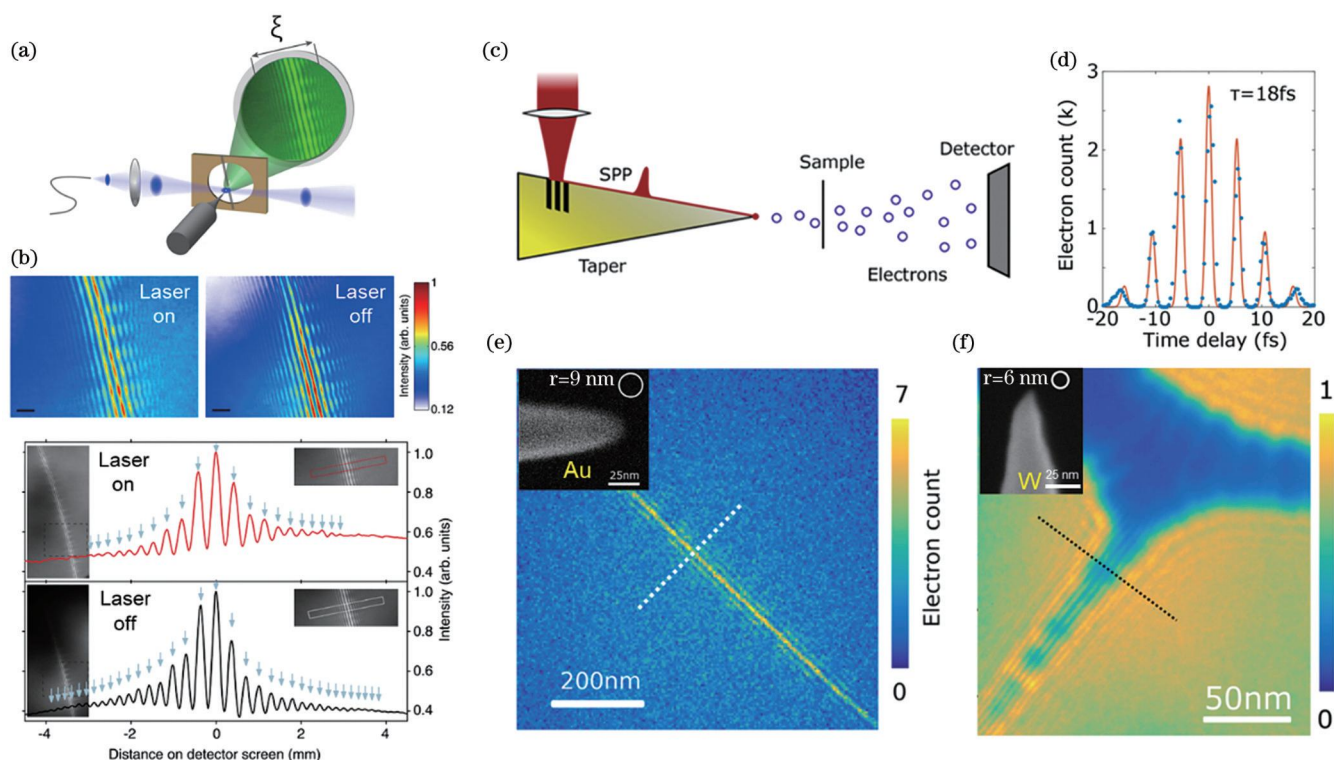


图 10 超快低能电子全息成像。(a)光电子发射及电子干涉实验原理^[38];(b)激光辐照前、后钨针尖场发射干涉条纹^[38];(c)超快电子全息成像原理^[37];(d)基于发射电流的脉冲自相关干涉测量^[37];(e)金针尖光电子发射干涉条纹^[37];(f)钨针尖光电子发射干涉条纹^[37]

Fig. 10 Ultrafast low-energy electron holography. (a) Experimental principle of photoelectron emission and electron interference^[38]; (b) tungsten tip field emission interference fringes before and after laser excitation^[38]; (c) schematic of ultrafast electron holography^[37]; (d) pulse autocorrelation interferometry based on emission current^[37]; (e) gold tip photoemission interference fringes^[37]; (f) tungsten tip photoemission interference fringes^[37]

两个针尖光电子发射均需工作在 MPP 机制下。根据观测到的碳管超快全息图像[图 10(e)、(f)]进行计算,金针尖和钨针尖的虚源半径分别为 4.7 nm 和 1.4 nm,对应的电子全息成像空间分辨率分别为 9.4 nm 和 2.8 nm。成像时间分辨率可达 18 fs[图 10(d)]。与上述 PFE 相比,MPP 机制提供的多光子能量与功函数的失配度更高。同时,激光功率高也会产生更强的热效应。这些因素都会导致电子源能量散度的提升。因此,文献^[37]中报道的虚源半径远大于文献^[38]中紫外光激发的超快相干电子源。

虽然研究人员通过优化激光参量改善了超快电子源的单色性,但基于传统金属针尖仍然很难实现静态场发射的相干性。因此,利用低维纳米材料在几何尺寸和电子结构方面的优势,构筑具有更高相干性的超快电子源是电子全息成像技术的一个重要发展趋势。

5 总结与展望

综上所述,超快低能电子全息成像技术在原子尺度电荷超快动力学表征方面展现出重要的应用前景。其成像的极限空间分辨能力主要由超快电子源的相干性决定。基于传统金属纳米针尖的超快电子源受物性限制,难以进一步提高相干性。相比之下,以碳管为代

表的低维纳米材料电子源具有原子尺度的发射位点和量子化的分立能级,是突破相干性瓶颈的重要基础。碳管具有丰富的碳体手性结构和尖端量子结构,为高性能电子源的优化设计带来了更多的调控维度。在未来,通过结合基于第一性原理的原子尺度材料设计和“自下而上”的原子制造技术,获得最优的碳管发射结构,有望获得接近不确定原理极限的超快电子源,进一步推动原子级分辨超快电子全息成像技术的发展。

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Ultrafast Low-Energy Electron Holography Based on Coherent Electron Source

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Abstract

Significance Solar energy utilization is crucial for all life on earth. For example, photosynthesis in green plants, which is vital for humans and other living creatures to have access to food, depends on solar energy. Furthermore, solar energy is the cleanest energy source and has various other applications, including solar-electric energy conversion through photovoltaics and solar-chemical energy through photosynthesis and photocatalysis. However, the conversion efficiency is currently low and needs to be improved. Therefore, the study of ultrafast dynamic processes at the atomic scale, such as carrier excitation, photoinduced charge separation, charge transfer, and energy transfer, is crucial for revealing the underlying physical mechanisms of photosynthesis, photovoltaic, and photocatalysis, which is significant for improving the conversion efficiency of solar energy.

Ultrafast electron microscopy is required to realize the high temporal-spatial resolution characterization of ultrafast dynamic processes. The ultrafast transmission electron microscope (TEM) and the ultrafast scanning electron microscope (SEM) have realized the real space observation of ultrafast dynamic processes at the nanoscale and atomic levels. These processes include atomic diffusion, chemical reaction, phase change, and biological macromolecular dynamics. Ultrafast TEM and ultrafast SEM typically use high-energy (>20 keV) electron beams for imaging. However, owing to the small scattering cross-section of high-energy electrons, the detection sensitivity to the weak local electric or optical field of the sample is low. Therefore, the transient charge transport process is challenging to characterize. In contrast, low-energy electrons with energy less than 500 eV have large scattering cross-section and scattering deflection angle for the weak local electric field in the sample and transient light field on the surface of nanostructures. Moreover, characterization with spatial resolution in the order of 10^{-10} m can be achieved via electron holography. Therefore, when combined with ultrafast temporal-resolution technology, the low-energy electron holography is expected to characterize the local electromagnetic field distribution and charge transport at the atomic level.

Point electron source projection microscope (referred to as “point projection”) is the simplest device to realize low-energy electron holography. By employing the laser-pumped ultrafast electron source, ultrafast low-energy electron holography can be achieved. Because matching the complex electron optical system is not needed, there is no aberration. The spatial resolution mainly depends on the electron source coherence. Therefore, an ultrafast coherent electron source is required to achieve ultrafast high spatial-resolution holography. In the past few years, many mechanisms to generate ultrafast electrons are discovered, including photon-assisted field emission (PFE), multiphoton photoemission (MPP), above-threshold photoemission (ATP), and optical field emission (OFE). Based on these mechanisms, ultrafast coherent electron sources have been built, and high temporal-spatial resolution holography has been achieved. Therefore, the current research is essential to guide the future development of this field more rationally.

Progress First, the fundamental mechanism of ultrafast electron sources is described in detail, and their coherence is discussed. The ultrafast electron source can be realized via laser pulse-modulated field emission. Photoelectron-emission mechanisms, including PFE, MPP, ATP, and OFE, generate ultrafast electron emission, which can achieve femtosecond or even up to sub-femtosecond

temporal resolution. Among these mechanisms, the electrons emitted under the PFE mechanism have a low-energy dispersion equivalent to the static field emission (Table 1), resulting to high coherence. Second, low-dimensional materials, such as one-dimension carbon nanotubes (Fig. 5) and zero-dimension quantum dots, have atomic-scale curvature radii and discrete energy levels induced via quantum confinement effect, enabling the high-coherent emitted electrons. Then, the influence of laser power, laser wavelength, radius of curvature, and discrete energy levels on electron source coherence is summarized, as shown in Table 2. Lastly, the development of static and ultrafast low-energy electron holography is introduced. Furthermore, based on high-coherent tungsten tip electron sources, static holographic imaging of single protein molecule, single DNA molecule, graphene lattice, and sub-nanometer scale charge state can be achieved. Using ultrafast electron sources, the sub-10 fs temporal resolution characterization of the ultrafast dynamic process of photogenerated carriers and nanogap charge transfer in semiconductor nanowires can be realized. However, the spatial resolution of electron holography can only reach several nanometers, as shown in Fig. 10, much larger than that in the static cases. The main reason is that the thermal effect, photon energy mismatch, and strong light field acceleration caused by femtosecond laser weaken the electron source coherence, reducing the spatial resolution of the ultrafast holography.

Conclusions and Prospects In conclusion, further improvement of ultrafast electron source coherence based on traditional metal nanotip is challenging owing to its physical property limitation. In contrast, low-dimensional nanomaterial electron sources, such as electron source based on carbon nanotubes, have atomic-scale emission sites and quantized discrete energy levels, which is an important basis for breaking the coherence bottleneck. Additionally, carbon nanotubes have rich carbon-chiral structures and cutting-edge quantum structures, bringing more regulatory dimensions for the optimal design of high-performance electronic sources. In the future, we will develop the optimal carbon tube emission structure by combining the atomic-scale material design based on the first principle and the “bottom-up” atomic manufacturing technology. This structure is expected to achieve an ultrafast electron source close to the uncertainty principle limit and promote the development of the atomic resolution of ultrafast electron holographic imaging technology.

Key words holography; electron holography; low-energy electron imaging; ultrafast electron source; coherent electron source; field emission; charge transport ultrafast dynamics