引用格式：FAN Renhao, HOU Benqi, PENG Ruwen, et al. Dynamically Tunable Optical Materials and Devices Based on Phase Transition of Vanadium Dioxide (Invited)[J]. Acta Photonica Sinica, 2022, 51(5):0551304
范仁浩，侯本颀，彭茹雯，等. 基于二氧化钒相变实现动态可调的亚波长光学材料和器件(特邀)[J]. 光子学报，2022，51(5)：0551304

基于二氧化钒相变实现动态可调的亚波长光学材料和器件(特邀)

范仁浩，侯本颀，彭茹雯，王牧
(南京大学 物理学院和固体微结构物理国家重点实验室，南京 210093)

摘 要：亚波长人工微纳结构，诸如超构材料和超构表面等，可以实现很多天然材料所不具备的新颖光学性质，为电磁波的操控提供有效手段。但基于静态结构而研制出的光学材料和器件往往只具有固定的光学功能，难以应对复杂多变的实际应用需求。近年来，人们将二氧化钒等相变材料引入人工微纳结构，实现了一系列可调光学材料和器件，其性能可实时改变和动态控制。本文回顾了二氧化钒的结构、相变机制及其物理特性等研究，展示了热、电、光等激发方式对二氧化钒相变的调控，系统总结了基于二氧化钒相变实现动态可调亚波长光学材料和器件的研究进展，期望推动发展新型亚波长动态可调的光电功能材料和器件。

关键词：超构材料；等离激元；动态调控；二氧化钒相变；超构表面
中图分类号：O436 **文献标识码**：A **doi**：10.3788/gzxb20225105.0551304

0 引言

由于自然界的材料对光的调控能力有限，近年来人们设计了一系列具有特殊光学参数的亚波长人工微纳结构，例如表面等离激元结构[1-7]、超构材料[8-11]、超构表面[12-16]等。这些人工微纳结构通过特定的形状设定与空间分布，可以使其对电磁波的响应按照人们的需求在亚波长尺度内被调制[17]，从而实现目前自然界中不存在的材料性质和新奇的物理现象，比如负折射现象[10,18-19]、光学隐身[20-23]、慢光效应[24-26]、宽带透明金属[27-29]，等等。然而，基于静态人工微纳结构而研制出的光学材料和器件往往具有固定的光学功能，难以应对复杂多变的实际应用需求。为了解决上述问题，人们引入了光学性能可调控的材料与人工微纳结构相结合，一些动态可调控的、可重构的光学材料和器件逐渐被人们设计和实现，使其能够在外部调控时主动控制电磁波[30-36]。这些光学性能可动态调节的材料包括可以调节载流子浓度的导电材料(如石墨烯[37-41]、半导体[42-43]、透明导电氧化物[44-46])，液晶[47-49]，聚合物[50-52]，非线性材料[53]，相变材料[54-57]等。人们通过机械调控[58-61]、电场、光场或温度场改变材料的光学参数，从而调节光的振幅、相位、偏振、角动量和传播方向等，进而实现对光学材料和器件的动态调控。这些动态可调控的光学材料和器件将不再局限于固定的光学响应，而可以根据实际的应用需求实时且动态地改变其光学功能，例如动态可调的等离激元结构色[62-65]、动态可调的偏振器[59,66-67]、动态可调的吸收器[68]、动态可调的全息[69]、动态可调的光波导器件[70]、动态可调的纳米天线[71-74]等。

在这些光学性能可动态调节的材料中，相变材料二氧化钒(Vanadium Dioxide，VO_2)近年来被人们逐渐关注[32,75-82]。二氧化钒的温度发生改变时会发生绝缘体-金属相变，同时晶体结构也由单斜结构转变成金红石结构[75,83]。除了常用的热激发二氧化钒相变[62,67,72]，人们也可以通过电场[84-85]、电流[66,68,71,86-88]、光场[89]、机

基金项目：国家自然科学基金(Nos. 11634005, 61975078, 11974177)，国家重点研发计划(No. 2017YFA0303702)
第一作者：范仁浩(1986—)，男，副教授，博士，主要研究方向为微纳光子学、太赫兹功能材料。 Email: rhfan@nju.edu.cn
通讯作者：彭茹雯(1967—)，女，教授，博士，主要研究方向为微纳光子学、微结构物理与功能材料。 Email: rwpeng@nju.edu.cn
收稿日期：2022-01-25；**录用日期**：2022-04-14

械力[90-93]、电化学[94]和磁场[95]等方式激发其相变[96]，其中热激发、电激发和光激发的二氧化钒相变比较适合用于调控电磁波。二氧化钒相变前后的力学、电学和光学性质都发生较大的变化，特别是二氧化钒相变前后折射率的变化非常明显[78,97-98]，因此适合与人工微纳结构相结合，实现基于二氧化钒相变的动态可调光学材料和器件。目前，二氧化钒已广泛应用于可调的光学材料和器件，例如纳米天线[71-72]、吸收器[68]、光存储器[99]、场效应晶体管[100]、调制器[101-102]、智能窗户[94,103]、波导开关[104-106]、等离激元结构色[62]、可调偏振器[66-67,107]等。

本文将首先介绍二氧化钒的晶体结构及其能带结构、相变机制、对电磁波的动态调控能力；接着介绍实现动态可调的光学材料和器件中常用到的三种二氧化钒相变的激发方式，具体包括基于热激发的二氧化钒相变、基于电激发的二氧化钒相变以及基于光激发的二氧化钒相变；然后总结几类基于二氧化钒结合人工微纳结构的可调光学材料和器件研究进展，具体包括：结合等离激元结构实现的可调光学材料和器件、结合超构材料或超构表面实现的可调光学材料和器件以及结合波导等结构实现的可调光学材料和器件；最后给出总结。

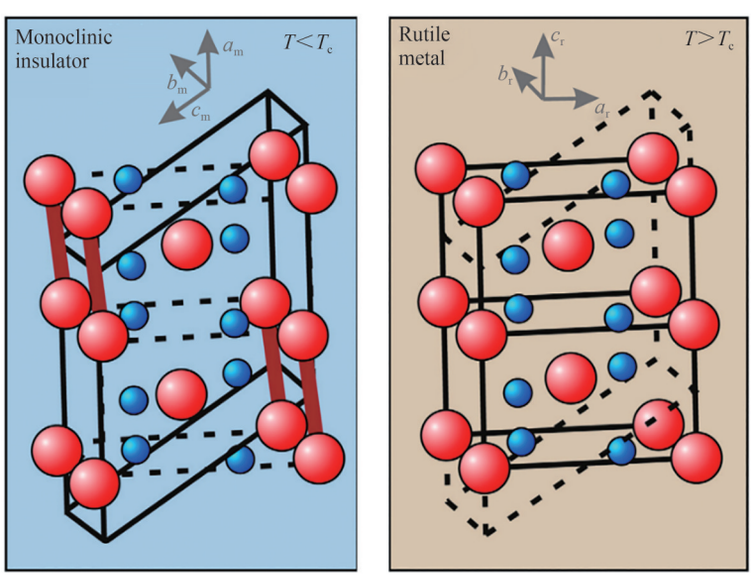
1 二氧化钒的介绍

1.1 二氧化钒的晶体结构及其能带结构

二氧化钒自1959年被MORIN F J发现以来引起了人们广泛的研究[108,75-76]。二氧化钒升温到68℃左右发生绝缘体-金属相变，其晶体结构由单斜结构转变成金红石结构[68,72]。如图1所示，相变温度以下时二氧化钒的晶体结构是单斜型结构，空间群为$P2_1/c$ (#14)，晶格常数$a \approx 0.575$ nm，$b \approx 0.453$ nm，$c \approx 0.538$ nm，$\beta = 122.6^\circ$，称为M1相；在相变温度以上时，二氧化钒的晶体结构是金红石型结构，空间群为$P4_2/mnm$ (#136)，晶格常数$a = b \approx 0.455$ nm，$c \approx 0.285$ nm，称为R相[76,109-110]。二氧化钒的这种晶格结构相变可以由实空间晶格向量变换矩阵给出[111]

$$\begin{pmatrix} a \\ b \\ c \end{pmatrix}_{M1} = \begin{pmatrix} 0 & 0 & 2 \\ 1 & 0 & 0 \\ 0 & 1 & \bar{1} \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix}_{R} \tag{1}$$

二氧化钒还具有另外两种晶体结构，一种称为M2相，属于单斜晶系，空间群为$C2/m$ (#12)；另一种称为T相，属于三斜晶系，空间群为$P\bar{1}$ (#2)，但是这两种晶体结构必须施加特定的应变条件或者掺杂Cr，W或Al等材料才能稳定存在[76]。二氧化钒的杨氏模量约为140 GPa，应变约为1%，其单位体积机械功输出高



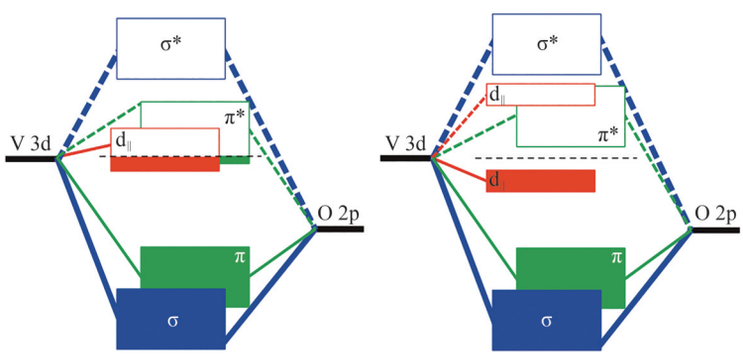
(a) Monoclinic VO_2 (b) Rutile VO_2

图1 二氧化钒的单斜型和金红石型晶体结构[109]

Fig. 1 Monoclinic and rutile crystal structures of vanadium dioxide[109]

达7 J/cm^3，因此二氧化钒适合用于可形变材料或驱动器材料[68,90-93,112]。

由于二氧化钒相变前后晶体结构发生改变，导致其对应的能带结构也会发生相应变化。GOODENOUGH J B最早研究了二氧化钒的能带结构[110,113]，如图2所示，二氧化钒结构的转变伴随着费米能级附近的电子能带的变化，可以通过一个晶体场模型定性地理解。当二氧化钒处于金红石结构时，其晶体的八面体结构以及O 2p轨道与V 3d轨道间的pd杂化，使得钒离子3d轨道分裂成相对高能量的e_g^σ对称态和相对低能量的t_{2g}对称态。由于局域晶体场的作用，t_{2g}态进一步分裂成两个d_π能带（π和π*）和一个$d_\parallel$能带，$d_\parallel$和π*能带均横跨费米面，因此二氧化钒呈现金属态。当二氧化钒转变为单斜结构时，由于结构扭曲，π*能带移动到费米能级之上，而$d_\parallel$形成成键态和反成键态，从而产生带隙，因此二氧化钒呈现绝缘态。



(a) Band structure in the metallic states　(b) Band structure in the insulating states

图2　二氧化钒处于金属态和绝缘态的能带结构[113]

Fig. 2　Band structure of vanadium dioxide in metallic and insulating states[113]

1.2　二氧化钒相变机制简介

基于二氧化钒相变前后晶体结构以及能带结构发生变化，人们一直致力于探索其相变的物理机制。二氧化钒相变过程中其结构转变改变了材料的能带结构，同时也伴随着较大的转变应力，但与其他相变材料不同的是，在二氧化钒的相变过程中这两种转变耦合在一起，似乎同时发生，这使得尽管二氧化钒已经被研究了60多年，但其相变机理一直长期存在着争议[75-76]。关于二氧化钒的相变机理长期存在两个理论：第一个是晶格扭曲导致的Peierls相变；第二个是电子关联导致的Mott相变。GOODENOUGH J B认为二氧化钒中强电子-声子相互作用导致了晶格扭曲，晶格扭曲使得其能带结构发生变化从而发生相变，此即为晶格扭曲导致的Peierls相变理论[110]。而MOTT N F等则认为二氧化钒中强电子关联导致能带结构发生变化，其能带结构变化又导致晶格扭曲从而发生相变，此即为电子关联导致的Mott相变理论[114]。

最近的理论处理倾向于在纯粹的Peierls相变理论和纯粹的Mott相变理论间找到关联和平衡点[76,115-118]。CAPELLO M等的计算表明了一种电子关联辅助的Peierls转变机制，表明电子间相互作用是二氧化钒能带打开的必要条件[115]。TOMCZAK J M等理论分析时同时考虑了电子间相互关联以及电子-声子相互作用，并将二氧化钒的绝缘态称为多体Peierls绝缘态[116]。WEBER C等基于线性标度密度泛函理论计算，并用非局部动态平均场理论改进，发现二氧化钒相变呈现出一种Peierls辅助的轨道选择性的Mott转变[118]。最近的一些实验研究也表明Peierls机制和Mott机制都对二氧化钒的相变起着重要的作用[119-122]。

1.3　二氧化钒对电磁波的动态调控能力

由于二氧化钒相变前后晶体结构以及能带结构发生变化，其相变过程中同时也会伴随着光吸收和介电函数的改变。以二氧化钒薄膜为例，目前二氧化钒薄膜可以通过多种方法来制备[77]，其中包括脉冲激光沉积[101]、溶胶凝胶法[99]、磁控溅射[88,123]和电子束蒸发[124]等。人们测量发现二氧化钒薄膜的折射率和介电函数从紫外、可见到红外波段随温度的变化而改变。例如在红外波段，当二氧化钒由绝缘体相转变成金属相后，其折射率的实部减少而虚部增加。基于相变前后折射率的较大变化，二氧化钒可以用于调控从紫外、可见

到红外波段的电磁波[62,66,68]。

而在太赫兹及微波波段，基于二氧化钒相变前后电阻的巨大变化，二氧化钒同样适合于调控电磁波。由于二氧化钒绝缘体-金属相变前后的能带结构发生较大变动，因此其电学性质也会随之改变，其特征是电导率的巨大变化。QAZILBASH M M等实验发现，当温度从341 K增加到344 K，二氧化钒薄膜的电阻减少了将近4个数量级[125]，如图3所示。在相变温度附近，由于二氧化钒的两相共存，其电阻随温度的变化是连续变化的，因此二氧化钒也适用于调控太赫兹和微波波段的电磁波。

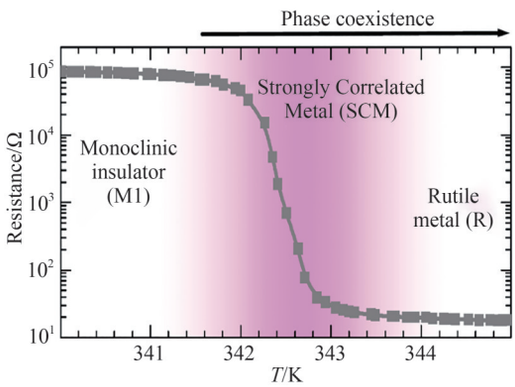


图3 二氧化钒薄膜相变过程中电阻随温度的变化关系[125]

Fig. 3 The phase diagram of a vanadium dioxide thin film and the resistance-temperature curve[125]

2 二氧化钒相变的激发方式

二氧化钒相变前后及相变过程中的折射率、介电函数、电阻等可以发生可逆及显著的变化，非常适合于通过外部刺激激发二氧化钒发生相变，从而动态调控电磁波。目前已经发现多种外部刺激可以激发二氧化钒的相变，比如：温度、光场、电场、电流、磁场、电化学和应力等[96]。其中热激发、电激发和光激发的二氧化钒相变适合于设计动态可调的光学材料和器件，并且得到了人们的广泛应用，因此这里重点介绍这三种二氧化钒相变的激发方式。

2.1 基于热激发的二氧化钒相变

任何有温度的物体都会产生热辐射，热辐射强度为[126]

$$I(K,T)=2hc\frac{K^3}{\mathrm{e}^{hcK/k_{\mathrm{B}}T}-1}\varepsilon(K) \tag{2}$$

式中，h为普朗克常数，c为光速，$K=f/c$为波数，f为频率，k_{B}为玻尔兹曼常数，T为温度，ε为发射系数。当温度改变时二氧化钒的吸收系数发生变化，根据基尔霍夫定律吸收系数等于发射系数，因此当温度改变时二氧化钒的热辐射也会发生变化[126-127]，因此二氧化钒薄膜可以用来调节热辐射，如图4所示。由于VO_2的相变温度T_{MIT}是可以在其制备的过程中通过掺杂的方式调节的[128]，常见的掺杂方式是在VO_2中引入钨(W)元素形成$W_xV_{1-x}O_2$合金，从而VO_2的相变温度将随W掺杂浓度的升高而降低，其定量关系为$\mathrm{d}T_{\mathrm{MIT}}(x)/\mathrm{d}x\approx-25$ ℃(当$T_{\mathrm{MIT}}>-100$ ℃时)[128]。人们可以根据实际的应用需求选择合适的掺杂浓度以实现二氧化钒在特定的温度发生金属-绝缘体相变，而相应地二氧化钒的热辐射也会随之发生改变。

基于热激发二氧化钒发生相变前后有较大的折射率和消光系数等变化，因此其可以用来设计一些温度调控的光学材料和器件[67,72,129-132]。例如，二氧化钒可以用于低功耗的智能窗户的设计[130]。当二氧化钒处于绝缘体相时，大部分红外光可以透过二氧化钒薄膜，室内温度较高；而当二氧化钒处于金属相时，只有少量红外光可以透过二氧化钒薄膜，室内温度较低。因此，基于二氧化钒相变可以实现对室内温度的动态调控。但是单纯二氧化钒薄膜室温下对太阳光的整体透过率的调制能力一般低于10%，为了进一步提高调制性能，可以通过二氧化钒结合人工微纳结构材料，例如多层二氧化钒结构、仿生结构、纳米热致变色结构、纳米多孔结构、网格结构等，如图5所示，以此进一步提高智能窗户的调制性能[96]。

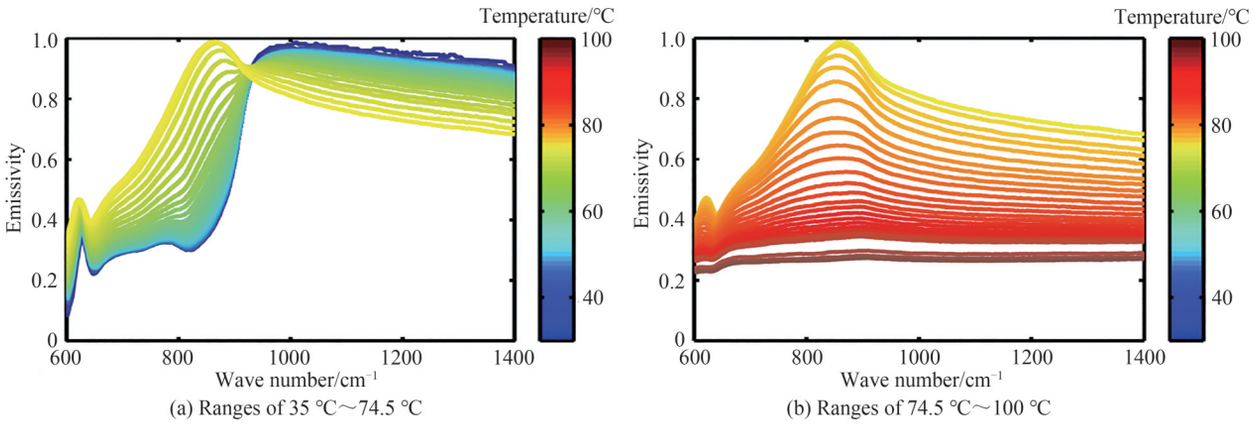


图 4　二氧化钒薄膜热辐射随温度的变化关系[126]

Fig. 4　Determined emissivity evolution of a vanadium dioxide thin film for increasing temperature[126]

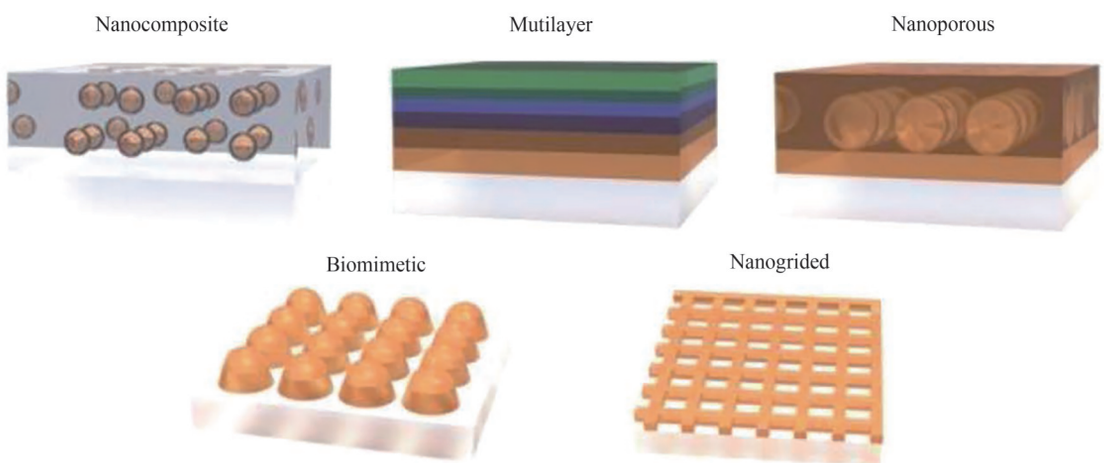


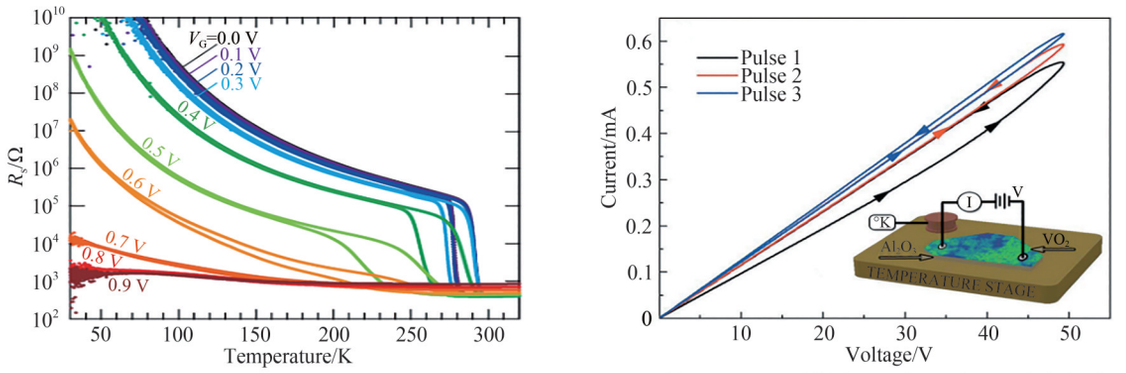
图 5　基于二氧化钒的智能窗户性能提高的五种方式[96]

Fig. 5　Typical structures effectively improve the performance of smart window based on vanadium dioxide[96]

2.2　基于电激发的二氧化钒相变

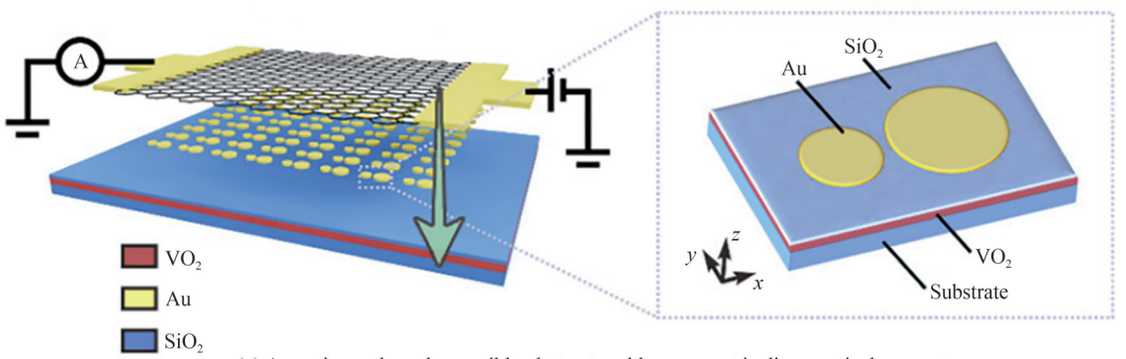
关于电激发二氧化钒相变，第一种方案是可以通过电场直接将电子或空穴注入到二氧化钒中，而不是通过热效应来诱导金属-绝缘体相变[94,133-139]，目前这种基于电场激发金属-绝缘体相变的物理机制仍然具有争议，尚待进一步研究[124]。例如，STEFANOVICH G 等利用场效应改变二氧化钒的载流子浓度来激发相变[124]，根据 Mott 相变理论[114]：$(n_c)^{1/3}\ \alpha_H \approx 0.25$，其中 n_c 为临界载流子浓度，α_H 为玻尔半径。当载流子浓度大于 n_c 时，二氧化钒由绝缘体相转变成金属相。再如，NAKANO M 等利用二氧化钒设计了金属-绝缘体-半导体场效应晶体管[138]。当施加电压时，二氧化钒表面的电荷积累促使体材料中载流子退局域，导致三维金属基态的出现，如图 6(a)所示，通过调控不同的门电压，可以对二氧化钒相变前后的电阻进行调控。另外，由于二氧化钒的电阻随电压的变化呈非线性，而且电阻随电压变化的曲线类似磁滞回线，如图 6(b)所示，因此其也可以用来实现忆阻器[136]。

关于电激发二氧化钒相变的第二种方案是施加电流产生焦耳热将二氧化钒加热到相变温度以上实现相变[66,71,140-143]。例如，WANG J N 等利用电流通过复合结构后产生焦耳热来激发二氧化钒的相变，如图 6(c)所示，当温度大于相变温度时也可以激发二氧化钒的绝缘体-金属相变，从而进行动态调控[71]。ZHANG C 等证明了电致热产生的二氧化钒相变和直接加热产生的二氧化钒相变，二者在机理和效果上是类似的，如图 6(d)所示[143]。

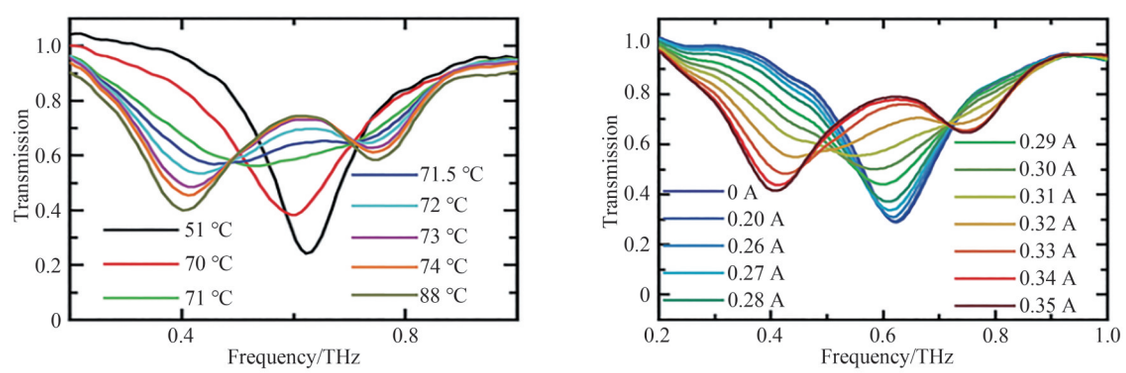


(a) The sheet resistance for a 10 nm VO_2 film with different gate voltages

(b) *I-V* curves exhibiting nonlinear hysteretic behavior



(c) A continuously and reversibly electro-tunable asymmetric dimer optical nanoantenna



(d) THz spectra at different temperatures spanning the transition temperature of the VO_2 thin film, and THz spectra at different bias currents at room temperature

图 6 基于电激发的二氧化钒相变[71,136,138,143]

Fig. 6 Phase transition of vanadium dioxide based on electrical excitation[71,136,138,143]

2.3 基于光激发的二氧化钒相变

关于光激发二氧化钒相变的研究工作根据其激发原理的不同主要分为两类[96]：第一类是基于超快动力学的光诱导相变，第二类则是利用光热效应。由于光热效应和直接加热效果类似不再罗列，这里重点介绍基于超快动力学的光诱导相变，其特征在于通过光激发使二氧化钒发生电子和空穴的重新分布，同时伴随着在飞秒到皮秒尺度内若干个非平衡态的产生[109,144-150]。CAVALLERI A等首先通过飞秒激光泵浦探测观察到二氧化钒超快相变[144]，相变时间与泵浦光的强度有关，当泵浦光的强度为25 mJ/cm^{2}时，二氧化钒经过100 fs后由绝缘体相转变成金属相，再经过几纳秒后又变回绝缘体相。BAUM P等通过四维电子衍射研究二氧化钒超快相变过程[146]，如图7所示，发现二氧化钒超快相变包含三个过程：第一步，从开始 t_i 时刻经过几百飞秒到 t_1 时刻，单斜结构中V-V二聚体被破坏；第二步，从 t_1 时刻经过10 ps到 t_2 时刻，单斜结构中V-V原子链被拉直；第三步，从 t_2 时刻经过几百皮秒到 t_f 时刻，晶体结构变成金红石结构。可见其相变速度大大快于接近秒量级的温控二氧化钒相变。MORRISON V R等结合超快电子衍射和红外透射分别探测二

氧化钒超快相变过程中晶体结构和载流子浓度的变化[148]，他们在超快相变过程中首次观察到一个中间态：晶体结构为单斜结构但红外光谱性质类似金属相。另外，WALL S等通过飞秒全X射线散射研究二氧化钒超快相变过程[150]，他们在超快相变过程中观察到无序现象，说明无序对二氧化钒超快相变也起重要作用。

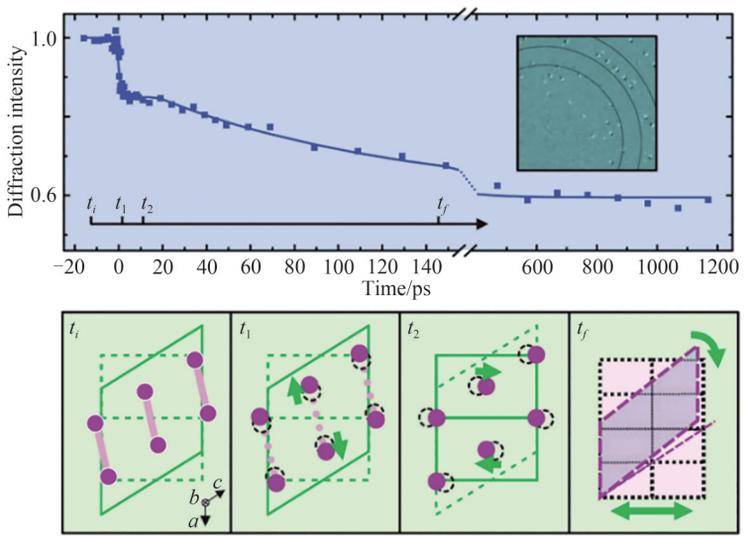


图7 通过四维电子衍射研究二氧化钒超快相变过程[146]

Fig. 7 Transitional structures in phase transformations of vanadium dioxide by electron diffraction[146]

3 基于二氧化钒的可调光学材料和器件

目前已经发现多种外部刺激可以激发二氧化钒的相变[96]，其中热激发、电激发和光激发的二氧化钒相变广泛应用于设计动态可调的光学材料和器件（如图8），解决了基于静态人工微纳结构而研制出的光学材料和器件往往只有固定光学功能的问题，使基于二氧化钒相变实现的动态可调光学材料和器件可以应对复杂多变的应用场景和器件多功能性的实际需求[75-79]。这里重点介绍几类结合人工微纳结构而实现的可调光学材料和器件。

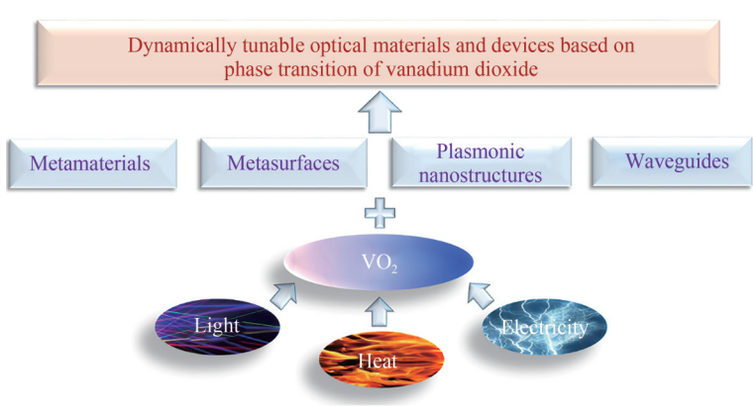


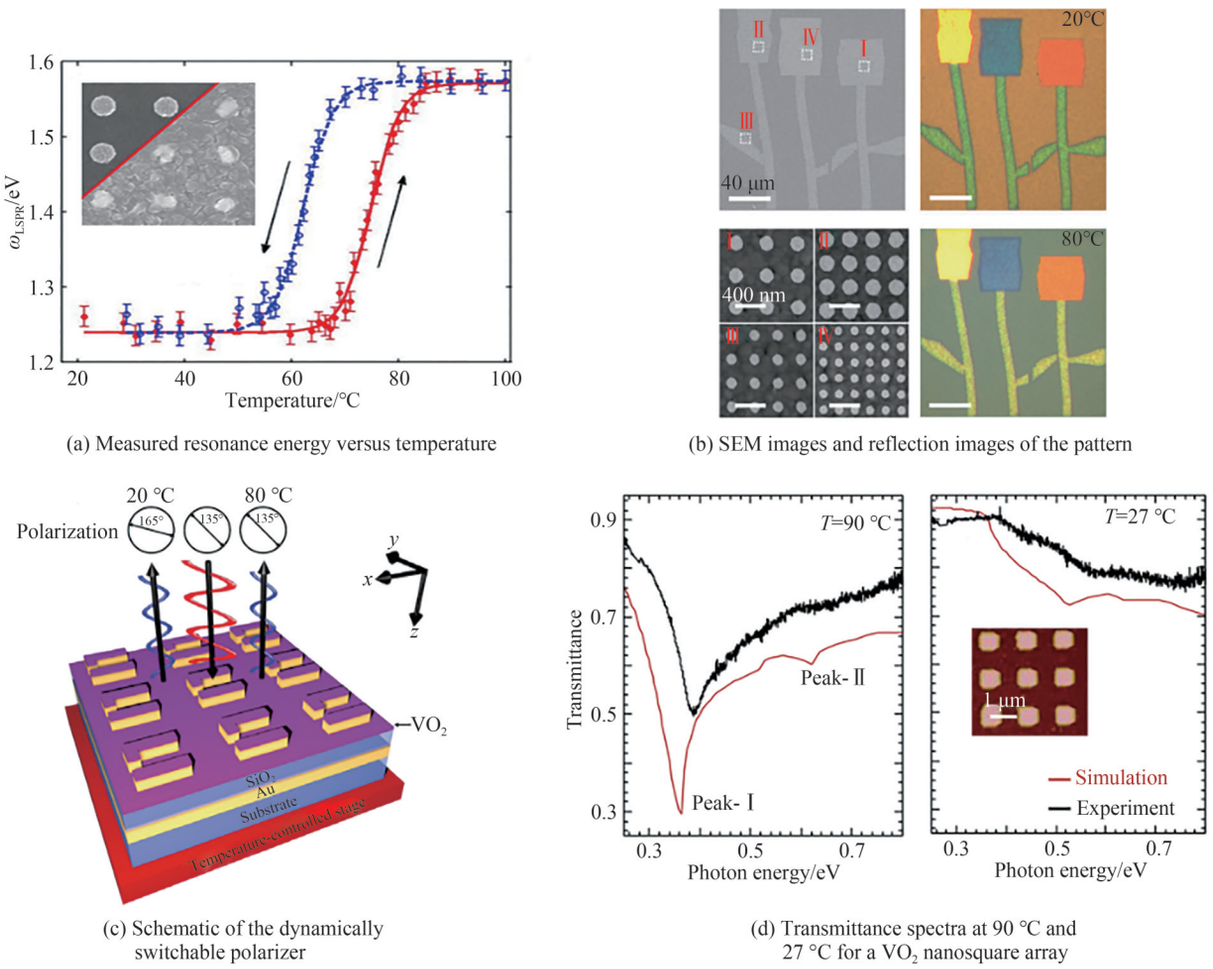
图8 基于二氧化钒相变实现动态可调的亚波长光学材料和器件

Fig. 8 Dynamically tunable optical materials and devices based on phase transition of vanadium dioxide

3.1 结合等离激元结构

表面等离激元是沿金属-介电材料或掺杂半导体-介电材料界面传播的电磁耦合模式[1-7]。当入射光照射金属表面时，金属表面的自由电子响应入射光电磁场的作用而产生集体振荡，这种表面电子的集体振荡和入射光之间的相互作用产生了表面等离激元，包括传播型表面等离激元和局域型表面等离激元。表面等离激元可以在纳米尺度实现光场的局域和增强[151-153]，将二氧化钒与等离激元纳米结构结合可以实现基于其相变的动态可调等离激元材料和器件[62,68,72,83,154-162]。由于表面等离激元对周围环境介电函数的变化比较敏感，因此基于二氧化钒相变前后介电函数的变化可以实现动态可调的等离激元材料和器件。例如，FERRARA

D W等在二氧化钒薄膜上设计金纳米颗粒阵列[83]，如图9(a)所示，当温度升高时，由于二氧化钒介电函数的变化，金纳米盘中局域型表面等离激元的共振频率也随之改变。SHU F Z等首次将等离激元纳米结构与二氧化钒结合实现动态可调的等离激元结构色[62]。该工作在二氧化钒薄膜上制备了周期性银纳米盘阵列，当光与其相互作用时会产生局域型和传播型表面等离激元，利用二氧化钒的绝缘体-金属转变性质，局域型和传播型表面等离激元的共振波长发生了变化，因此样品的颜色也随之改变，如图9(b)。



(a) Measured resonance energy versus temperature

(b) SEM images and reflection images of the pattern

(c) Schematic of the dynamically switchable polarizer

(d) Transmittance spectra at 90 ℃ and 27 ℃ for a VO_2 nanosquare array

图9 二氧化钒结合等离激元结构实现的可调光学材料和器件[62,67,83,157]

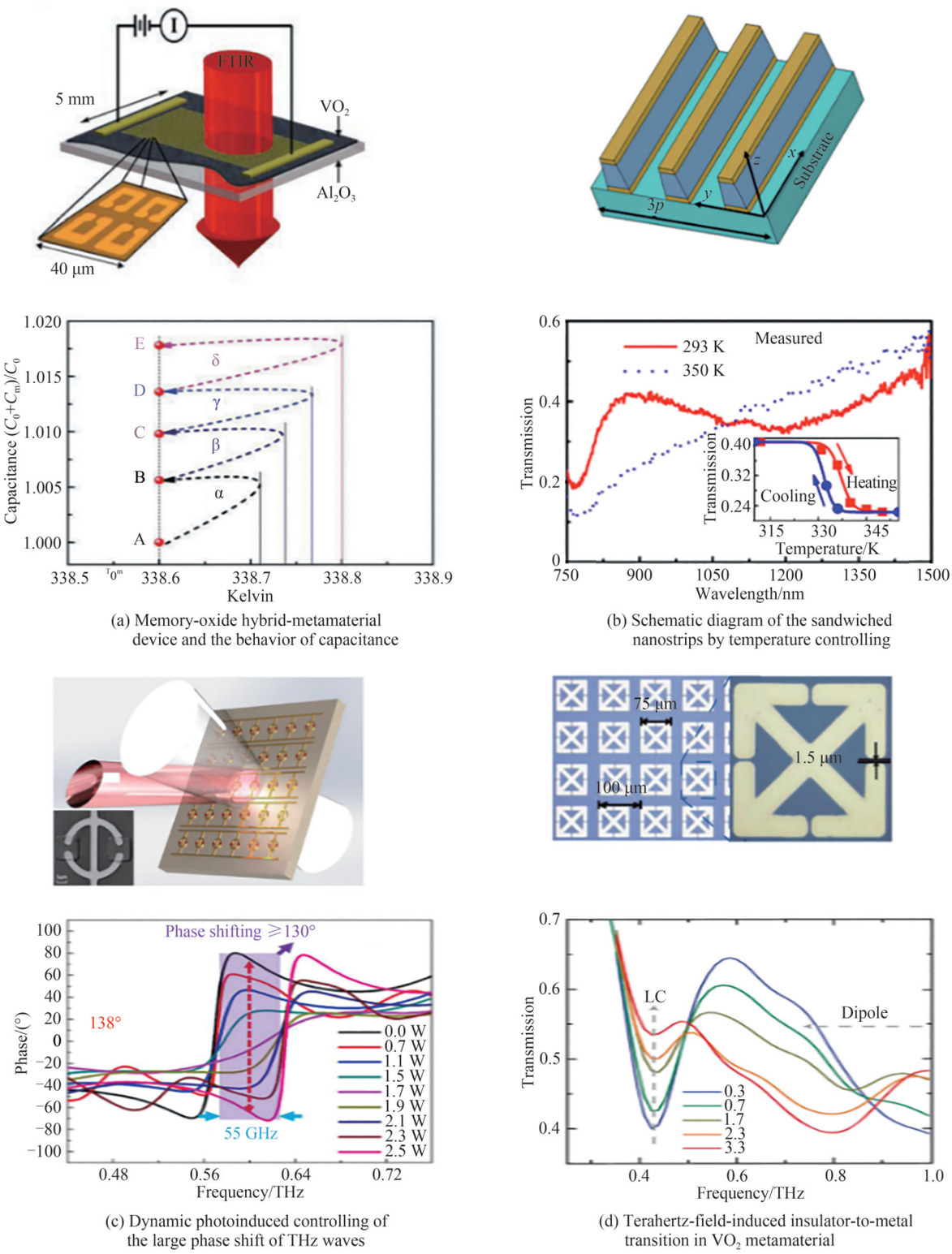
Fig. 9 Tunable optical materials and devices realized by vanadium dioxide combined with plasmonic structures[62,67,83,157]

由于二氧化钒高温相变后具有金属性，因此也可以将它与纳米结构相结合制成复合结构，从而实现材料和器件的动态调控[67,157,162]。JIA Z Y等将各向异性的等离激元纳米结构与二氧化钒结合，如图9(c)所示，实验证实在135°线偏振光入射下，改变温度可以动态调节各向异性纳米结构的反射和吸收，从而二氧化钒在常温绝缘体相下实现将波长为3 μm反射光的线偏振方向旋转到165°，而在高温下仅充当镜面反射效果，线偏振方向保持不变[67]。也可以直接用二氧化钒制成纳米结构，通过相变后具有金属性的纳米结构来激发表面等离激元并对其进行动态调控。例如，MATSUI H等将二氧化钒制成周期性纳米方块阵列[157]，如图9(d)。当二氧化钒处于金属相时，纳米方块结构可以激发表面等离激元模式并使不同方块的表面等离激元间发生共振耦合；而当二氧化钒处于绝缘体相时，纳米方块结构则无法激发表面等离激元模式。

3.2 结合超构材料或超构表面

超构材料首先是由英国物理学家PENDRY J B提出的[8-9]，主要思想是用具有特殊电磁响应的人工微纳结构单元取代晶体材料中的原子，当波长远大于结构周期时，人们可以忽略结构的细节，将其看作一个块体材料，从而构造出具有特殊介电常数ε和磁导率μ的材料，因而超构材料具备常规材料所没有的一些优异特性[8-11,163-165]。由于超构材料对周围环境介电函数的变化也比较敏感，因此基于二氧化钒相变前后介电函数的变

化可以实现动态可调的超构材料[71,85,99,166-177]。例如，DRISCOLL T等在二氧化钒薄膜上设计开口环结构[99]，如图10(a)。当对样品施加电压时，电流产生的焦耳热激发二氧化钒相变。二氧化钒的电阻发生变化，开口环的电容也随之改变，因此可用来实现存储器。此外，HUANG W X等将二氧化钒插入到平行金属条中构造了一种金属/绝缘体/金属三明治结构[167]，如图10(b)。当二氧化钒处于绝缘体相时，平行金属条之间相互耦合可以激发磁共振；而当二氧化钒处于金属相时，平行金属条之间导通无法激发磁共振。另外，ZHAO Y等提出了一种嵌套有



(a) Memory-oxide hybrid-metamaterial device and the behavior of capacitance

(b) Schematic diagram of the sandwiched nanostrips by temperature controlling

(c) Dynamic photoinduced controlling of the large phase shift of THz waves

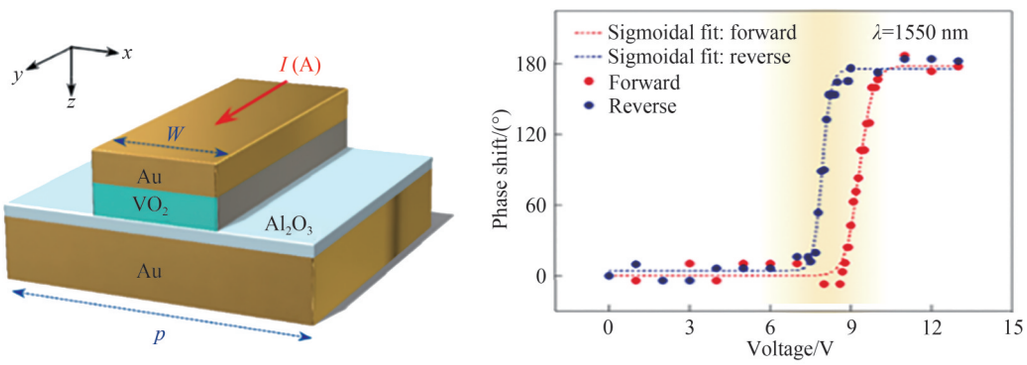
(d) Terahertz-field-induced insulator-to-metal transition in VO_2 metamaterial

图10　二氧化钒结合超构材料实现的可调光学材料和器件[85,99,167,175]

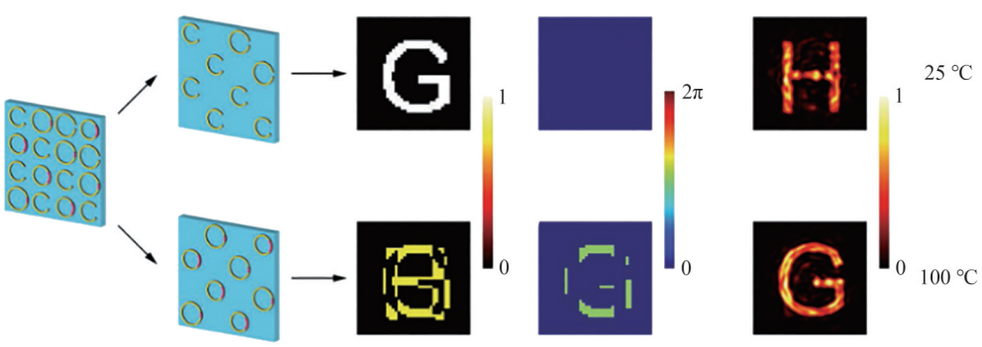
Fig. 10　Tunable optical materials and devices realized by vanadium dioxide combined with metamaterials[85,99,167,175]

二氧化钒纳米结构的环形哑铃复合谐振器[175]，利用二氧化钒相变过程中的折射率变化动态调控谐振器的共振频率，从而实现高达138°的大相位变化，如图10(c)。除了利用二氧化钒的相变来动态调节超构材料，也可以反过来利用超构材料激发二氧化钒的相变。比如，LIU M等在二氧化钒薄膜上设计了一种开口环结构[85]，如图10(d)。当飞秒太赫兹脉冲入射到样品上时，开口环间隙处的场增强效应使得二氧化钒由绝缘体相转变成金属相。

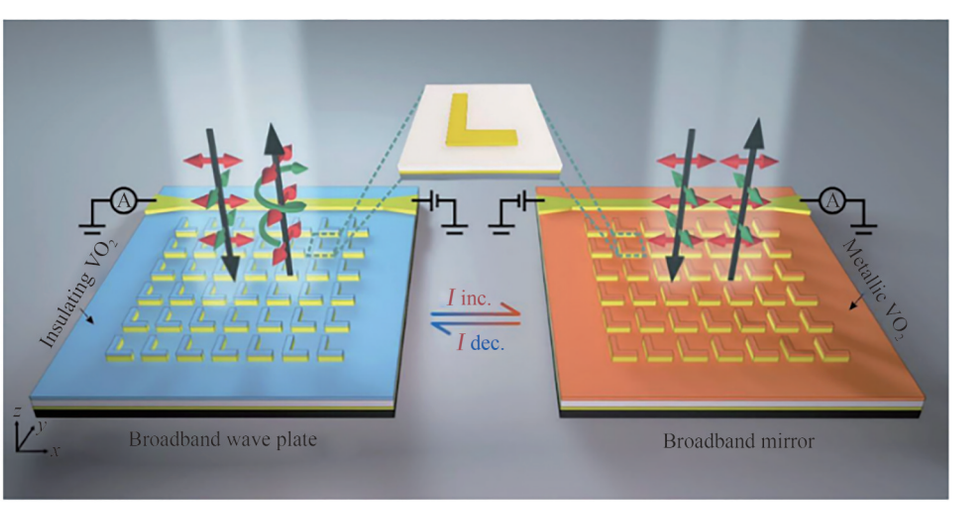
超构表面是一种特殊的二维超构材料，通常超构表面由超薄的亚波长人工微纳结构按照特定的顺序排列组成，人们可以使超构表面对反射或透射电磁波呈现出任意的相位和幅度分布，从而实现对电磁波的相位、振幅、传播方向以及偏振等性质的调制[12-16,178-181]。将二氧化钒与超构表面相结合也可以实现基于其相变的动态可调超构表面[66,69,71,182-193]。KIM Y等利用电压控制二氧化钒的逐渐相变，从而改变超构表面结构的磁偶极共振，达到一个相位的连续调控，如图11(a)所示，制备出位相调制器[187]。LIU X等将金属“C”型环超



(a) Phase modulation with electrically tunable VO_2 phase-change metasurfaces



(b) Design mechanism of the proposed thermal dynamic meta-hologram



(c) Schematic of electrically driven tunable broadband polarization states

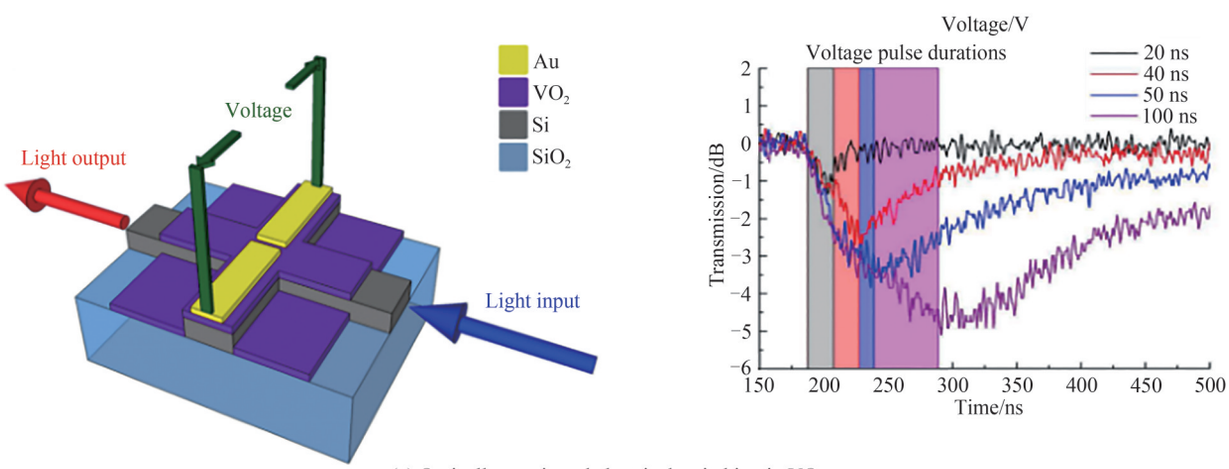
图11 二氧化钒结合超构表面实现的可调光学材料和器件[66,69,187]

Fig. 11 Tunable optical materials and devices realized by vanadium dioxide combined with metasurfaces[66,69,187]

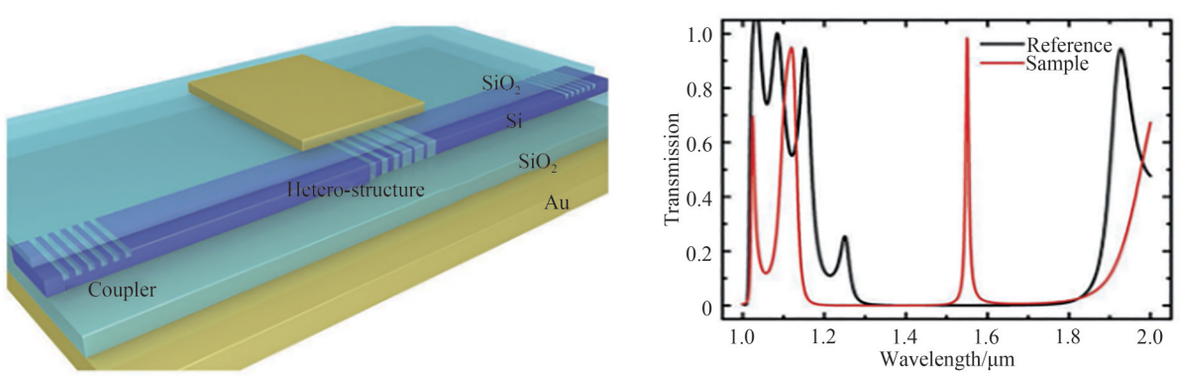
构表面与添加了二氧化钒的金属“C”型环超构表面嵌套，形成温度依赖的全息成像[69]。高温下添加了二氧化钒的“C”型环超构表面透过率很低不起作用，只有“C”型环超构表面起作用从而成“G”型全息成像；而常温下两种结构的位相和强度一致，均起作用从而形成“H”型全息成像，如图11(b)。SHU F Z等将可以调控入射光偏振态的“L”型超构表面与二氧化钒相结合，利用电致焦耳热实现二氧化钒的相变。常温下形成金属-介质-金属三明治结构，这样金属镜面对光的反射相当于形成了一个金属结构的镜像，金属结构和它镜像的辐射存在共轭关系，可以利用共轭关系来抵消金属的色散，从而实现宽频无色散的四分之一波片，如图11(c)所示，而高温下样品整体起宽带镜面的效果，入射线偏振态不改变[66]。KEPIČ P等则直接利用二氧化钒来做介质超构表面单元，由于相变前后折射率改变变化，因此可以温控实现对周围介质环境敏感的Mie共振及等离激元共振波长的调控[192]。

3.3 结合波导等结构

波导结构是一种重要的光学器件[4,194-196]，二氧化钒结合波导结构可以实现可调的光波导器件[70,78,104-106,197]。例如，MARKOV P等在硅波导上覆盖一层二氧化钒[105]，如图12(a)。未加电压时二氧化钒处于绝缘体相，其介电函数的虚部较小，光可以在波导中传输；当施加电压后二氧化钒转变成金属相，其介电函数的虚部较大，光不能在波导中传输，因此基于二氧化钒相变可以实现波导的开关。再例如，LI C等利用热控的VO_2/SiO_2光子晶体异质结构来实现光子拓扑边界态的开/关切换，如图12(b)所示，当二氧化钒处于绝缘体相时，结构等效为VO_2/SiO_2光子晶体，拓扑边界态可以产生并通过该波导传输；而当二氧化钒处于金属相时，光则直接被反射从而断开光路[106]。此外，光栅结构的应用也很广泛，CAI J等在石英衬底上制备了二氧化钒光栅结构，如图12(c)所示，实现了一种宽频带的太赫兹色散光束偏转器，可以在不同温度下实现三种功能的切换[198]。在室温25 ℃下，由于石英和二氧化钒的反射率差别很小，该器件呈现出基于介质表面的镜面反射器；当处于相变中的温度59 ℃时，两种不同折射率材料形成了二元相位板，可以实现不同波长对应不同偏转角的“彩虹”偏转器；当处于高温62 ℃时，由于二氧化钒处于金属相，该器件呈现出金属光栅状态。



(a) Optically monitored electrical switching in VO_2



(b) Tunable ultracompact chip-integrated 1D photonic topological insulator

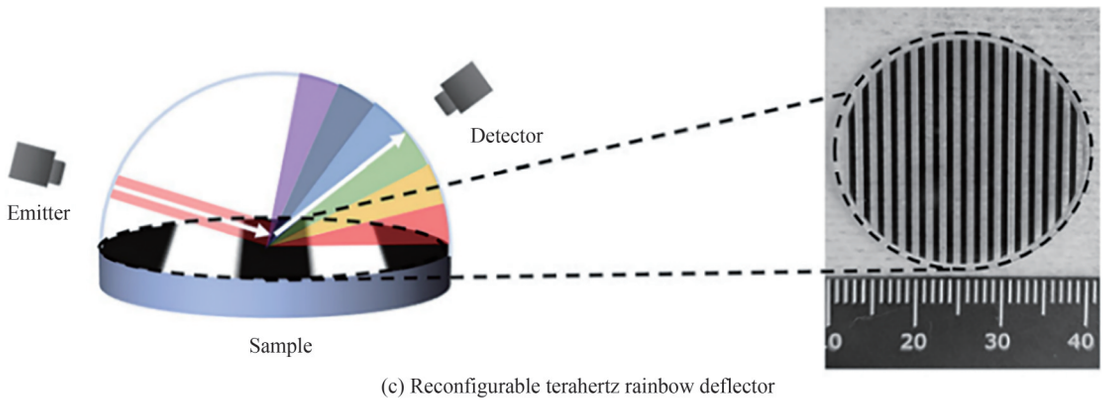


图 12 二氧化钒结合波导等结构实现的可调光学材料和器件[105-106,198]

Fig. 12 Tunable optical materials and devices realized by vanadium dioxide combined with waveguides or gratings[105-106,198]

4 结论

本文首先介绍了当温度改变时二氧化钒会发生绝缘体-金属相变，其晶体结构由单斜结构转变成金红石结构，以及其对应的金属态和绝缘态的能带结构之间的转变。接着概述了二氧化钒的相变机理长期存在的两个理论：一是晶格扭曲导致的Peierls相变；二是电子关联导致的Mott相变。目前理论处理倾向于在纯粹的Peierls相变理论和纯粹的Mott相变理论间找到关联和平衡点。然后介绍了基于相变前后折射率的较大变化，二氧化钒可以用于调控从紫外、可见到红外波段的电磁波；而在太赫兹及微波波段，是基于二氧化钒相变前后电阻的巨大变化来调控电磁波。接着介绍了热激发、电激发和光激发这三种适合于设计动态可调的光学材料和器件的二氧化钒相变的激发方式。最后重点综述几类结合人工微纳结构而实现的可调光学材料和器件，包括结合等离激元结构实现的可调光学材料和器件、结合超构材料或超构表面实现的可调光学材料和器件以及结合波导等结构实现的可调光学材料和器件。未来基于二氧化钒的动态可调光学器件还可以在很多方向继续研究，其中包括：1)氧原子和钒原子还可以形成其他组分的氧化物，其中有些组分的化合物也具有温度控制的相变，例如：V_2O_3、V_3O_5、V_4O_7、V_5O_9、V_6O_{11}、V_8O_{15}等，这些氧化物也具有类似VO_2的相变曲线，因此也可以利用其他组分的氧化钒化合物与人工微纳结构单元结合来实现动态调控的光学器件；2)目前大部分器件用的是二氧化钒相变前后的状态，如果充分利用相变过程中的中间态，人们可以实现多种功能的集成；3)将二氧化钒材料与人工微纳结构相集成，可以研制更多的动态可调控的光电材料和器件；等等。期望相关研究能够推动新型亚波长动态可调的光电功能材料和器件的发展。

参考文献

[1] XU H, BJERNELD E J, KÄLL M, et al. Spectroscopy of single hemoglobin molecules by surface enhanced Raman scattering[J]. Physical Review Letters, 1999, 83(21): 4357-4360.

[2] BARNES W L, DEREUX A, EBBESEN T W. Surface plasmon subwavelength optics[J]. Nature, 2003, 424(6950): 824-830.

[3] SCHULLER J A, BARNARD E S, CAI W, et al. Plasmonics for extreme light concentration and manipulation[J]. Nature Materials, 2010, 9(3): 193-204.

[4] WEI H, HAO F, HUANG Y, et al. Polarization dependence of surface-enhanced Raman scattering in gold nanoparticle-nanowire systems[J]. Nano Letters, 2008, 8(8): 2497-2502.

[5] CHEN Y H, HUANG L, GAN L, et al. Wavefront shaping of infrared light through a subwavelength hole[J]. Light: Science & Applications, 2012, 1: e26.

[6] TANG Z H, PENG R W, WANG Z, et al. Coupling of surface plasmons in nanostructured metal/dielectric multilayers with subwavelength hole arrays[J]. Physical Review B, 2007, 76(19): 195405.

[7] BAO Y J, PENG R W, SHU D J, et al. Role of interference between localized and propagating surface waves on the extraordinary optical transmission through a subwavelength-aperture array[J]. Physical Review Letters, 2008, 101(8): 087401.

[8] PENDRY J B, HOLDEN A J, STEWART W J, et al. Extremely low frequency plasmons in metallic mesostructures[J]. Physical Review Letters, 1996, 76(25): 4773-4776.

[9] PENDRY J B, HOLDEN A J, ROBBINS D J, et al. Magnetism from conductors and enhanced nonlinear phenomena[J].

IEEE Transactions on Microwave Theory and Techniques,1999, 47(11): 2075-2084.
[10] XIAO S, DRACHEV V P, KILDISHEV A V, et al. Loss-free and active optical negative-index metamaterials[J]. Nature, 2010, 466(7307): 735-738.
[11] JIANG S C, XIONG X, HU Y S, et al. Controlling the polarization state of light with a dispersion-free metastructure[J]. Physical Review X, 2014, 4(2): 021026.
[12] YU N, GENEVET P, KATS M A, et al. Light propagation with phase discontinuities: generalized laws of reflection and refraction[J]. Science, 2011, 334(6054): 333-337.
[13] SUN S, HE Q, XIAO S, et al. Gradient-index meta-surfaces as a bridge linking propagating waves and surface waves [J]. Nature Materials, 2012, 11(5): 426-431.
[14] KILDISHEV A V, BOLTASSEVA A, SHALAEV V M. Planar photonics with metasurfaces[J]. Science, 2013, 339 (6125): 1232009.
[15] CHEN S, LI Z, LIU W, et al. From single-dimensional to multidimensional manipulation of optical waves with metasurfaces[J]. Advanced Materials, 2019, 31(16): 1802458.
[16] GAO Y J, XIONG X, WANG Z H, et al. Simultaneous generation of arbitrary assembly of polarization states with geometrical-scaling-induced phase modulation[J]. Physical Review X, 2020, 10(3): 031035.
[17] FAN R H, XIONG B, PENG R W, et al. Constructing metastructures with broadband electromagnetic functionality[J]. Advanced Materials, 2020, 32(27): 1904646.
[18] SHELBY R A, SMITH D R, SCHULTZ S. Experimental verification of a negative index of refraction[J]. Science, 2001, 292(5514): 77-79.
[19] XIONG X, SUN W H, BAO Y J, et al. Construction of a chiral metamaterial with a U-shaped resonator assembly[J]. Physical Review B, 2010 81(7): 075119.
[20] PENDRY B, SCHURIG D, SMITH D R. Controlling electromagnetic fields[J]. Science, 2006, 312(5781): 1780-1782.
[21] ZHAO J Z, WANG D L, PENG R W, et al. Watching outside while under a carpet cloak of invisibility[J]. Physical Review E, 2011, 84(4): 046607.
[22] LIU D, HONG Y L, FAN R H, et al. Bendable disordered metamaterials for broadband terahertz invisibility[J]. Optics Express, 2020, 28(3): 3552-3560.
[23] LUO J, CHU H C, PENG R W, et al. Ultra-broadband reflectionless Brewster absorber protected by reciprocity[J]. Light- Science & Applications, 2021, 10(1): 89.
[24] ZHANG S, GENOV D A, WANG Y, et al. Plasmon-induced transparency in metamaterials[J]. Physical Review Letters, 2008, 101(4): 047401.
[25] QIN L, ZHANG K, PENG R W, et al. Optical-magnetism-induced transparency in a metamaterial[J]. Physical Review B, 2013, 87(12): 125136.
[26] ZHANG K, WANG C, QIN L, et al. Dual-mode electromagnetically induced transparency and slow light in a terahertz metamaterial[J]. Optics Letters, 2014, 39(12): 3539-3542.
[27] HUANG X R, PENG R W, FAN R H. Making metals transparent for white light by spoof surface plasmons[J]. Physical Review Letters, 2010, 105(24): 243901.
[28] FAN R H, PENG R W, HUANG X R, et al. Transparent metals for ultrabroadband electromagnetic waves[J]. Advanced Materials, 2012, 24(15): 1980-1986.
[29] FAN R H, LI J, PENG R W, et al. Oblique metal gratings transparent for broadband terahertz waves[J]. Applied Physics Letters, 2013, 102(17): 171904.
[30] ZHELUDEV N I, KIVSHAR Y S. From metamaterials to metadevices[J]. Nature Materials, 2012, 11(11): 917-924.
[31] NEMATI A, WANG Q, HONG M, et al. Tunable and reconfigurable metasurfaces and metadevices[J]. Opto-Electronic Advances, 2018, 1(5): 180009.
[32] SHU F Z, FAN R H, WANG J N, et al. Advances in dynamically tunable plasmonic materials and devices[J]. Acta Physica Sinica, 2019, 68(14): 147303.
[33] HE Q, SUN S, ZHOU L. Tunable/reconfigurable metasurfaces: physics and applications[J]. Research, 2019, 2019(2): 1849272.
[34] CHE Y, WANG X, SONG Q, et al. Tunable optical metasurfaces enabled by multiple modulation mechanisms[J]. Nanophotonics, 2020, 9(15): 4407-4431.
[35] CHENG H, CHEN S, YU P, et al. Dynamically tunable broadband infrared anomalous refraction based on graphene metasurfaces[J]. Advanced Optical Materials, 2015, 3(12): 1744-1749.
[36] XIONG B, XU Y H, WANG J N, et al. Realizing colorful holographic mimicry by metasurfaces[J]. Advanced Materials, 2021, 33(21): 2005864.
[37] EMANI N K, CHUNG T F, NI X, et al. Electrically tunable damping of plasmonic resonances with graphene[J]. Nano

Letters, 2012, 12(10): 5202-5206.
[38] YAO Y, KATS M A, GENEVET P, et al. Broad electrical tuning of graphene-loaded plasmonic antennas[J]. Nano Letters, 2013, 13(3): 1257-1264.
[39] CHENG H, CHEN S, YU P, et al. Dynamically tunable broadband mid-infrared cross polarization converter based on graphene metamaterial[J]. Applied Physics Letters, 2013, 103(22): 223102.
[40] ZHOU Y, WANG C, XU D H, et al. Tuning the dispersion relation of a plasmonic waveguide via graphene contact[J]. Europhysics Letters, 2014, 107(3): 34007.
[41] ZHOU Y, DONG Y Q, FAN R H, et al. Asymmetric transmission of terahertz waves through a graphene-loaded metal grating[J]. Applied Physics Letters, 2014, 105(4): 041114.
[42] CHEN H T, PADILLA W J, ZIDE J M O, et al. Active terahertz metamaterial devices[J]. Nature, 2006, 444(7119): 597-600.
[43] JING H, PENG R W, MA R M, et al. Flexible ultrathin single-crystalline perovskite photodetector[J]. Nano Letters, 2020, 20(10): 7144-7151.
[44] HUANG Y W, LEE H W H, SOKHOYAN R, et al. Gate-tunable conducting oxide metasurfaces[J]. Nano Letters, 2016, 16(9): 5319-5325.
[45] PARK J, KANG J H, KIM S J, et al. Dynamic reflection phase and polarization control in metasurfaces[J]. Nano Letters, 2017, 17(1): 407-413.
[46] ALAM M Z, SCHULZ S A, UPHAM J, et al. Large optical nonlinearity of nanoantennas coupled to an epsilon-near-zero material[J]. Nature Photonics, 2018, 12(2): 79-83.
[47] WANG X, KWON D H, WERNER D H, et al. Tunable optical negative-index metamaterials employing anisotropic liquid crystals[J]. Applied Physics Letters, 2007, 91(14): 143122.
[48] CETIN A E, MERTIRI A, HUANG M, et al. Thermal tuning of surface plasmon polaritons using liquid crystals[J]. Advanced Optical Materials, 2013, 1(12): 915-920.
[49] ABASS A, RODRIGUEZ S R, AKO T, et al. Active liquid crystal tuning of metallic nanoantenna enhanced light emission from colloidal quantum dots[J]. Nano Letters, 2014, 14(10): 5555-5560.
[50] REN M X, WU W, CAI W, et al. Reconfigurable metasurfaces that enable light polarization control by light[J]. Light: Science & Applications, 2017, 6: e16254.
[51] ZHANG K, SHI W B, WANG D, et al. Couple molecular excitons to surface plasmon polaritons in an organic-dye-doped nanostructured cavity[J]. Applied Physics Letters, 2016, 108(19): 193111.
[52] XIONG B, WANG J N, PENG R W, et al. Construct achromatic polymer microlens for high-transmission full-color imaging[J]. Advanced Optical Materials, 2020, 9(2): 2001524.
[53] NICHOLLS L H, RODŔIGUEZ-FORTUÑO F J, NASIR M E, et al. Ultrafast synthesis and switching of light polarization in nonlinear anisotropic metamaterials[J]. Nature Photonics, 2017, 11(10): 628-633.
[54] YIN X, SCHÄFERLING M, MICHEL A K U, et al. Active chiral plasmonics[J]. Nano Letters, 2015, 15(7): 4255-4260.
[55] WANG Q, ROGERS E T F, GHOLIPOUR B, et al. Optically reconfigurable metasurfaces and photonic devices based on phase change materials[J]. Nature Photonics, 2016, 10(1): 60-65.
[56] TITTL A, MICHEL A U, SCHÄFERLING M, et al. A switchable mid-infrared plasmonic perfect absorber with multispectral thermal imaging capability[J]. Advanced Materials, 2015, 27(31): 4597-4603.
[57] TIAN J, LUO H, YANG Y, et al. Active control of anapole states by structuring the phase-change alloy $Ge_2Sb_2Te_5$[J]. Nature Communications, 2019, 10: 396.
[58] GAO F, LI D, PENG R W, et al. Tunable interference of light behind subwavelength apertures[J]. Applied Physics Letters, 2009, 95(1): 011104.
[59] FAN R H, ZHOU Y, REN X P, et al. Freely tunable broadband polarization rotator for terahertz waves[J]. Advanced Materials, 2015, 27(7): 1201-1206.
[60] ZHELUDEV N I, PLUM E. Reconfigurable nanomechanical photonic metamaterials[J]. Nature Nanotechnology, 2016, 11(1): 16-22.
[61] WANG Z, JING L, YAO K, et al. Origami-based reconfigurable metamaterials for tunable chirality[J]. Advanced Materials, 2017, 29(27): 1700412.
[62] SHU F Z, YU F F, PENG R W, et al. Dynamic plasmonic color generation based on phase transition of vanadium dioxide [J]. Advanced Optical Materials, 2018, 6(7): 1700939.
[63] XU T, WALTER E C, AGRAWAL A, et al. High-contrast and fast electrochromic switching enabled by plasmonics [J]. Nature Communications, 2016, 7: 10479.
[64] DUAN X, KAMIN S, LIU N. Dynamic plasmonic colour display[J]. Nature Communications, 2017, 8: 14606.
[65] TSENG M L, YANG J, SEMMLINGER M, et al. Two-dimensional active tuning of an aluminum plasmonic array for

full-spectrum response[J]. Nano Letters 2017, 17(10): 6034-6039.
[66] SHU F Z, WANG J N, PENG R W, et al. Electrically driven tunable broadband polarization states via active metasurfaces based on joule-heat-induced phase transition of vanadium dioxide[J]. Laser & Photonics Reviews, 2021, 15(10): 2100155.
[67] JIA Z Y, SHU F Z, GAO Y J, et al. Dynamically switching the polarization state of light based on the phase transition of vanadium dioxide[J]. Physical Review Applied, 2018, 9(3): 034009.
[68] WANG J N, XIONG B, PENG R W, et al. Flexible phase change materials for electrically-tuned active absorbers[J]. Small, 2021, 17(31): 2101282.
[69] LIU X, WANG Q, ZHANG X, et al. Thermally dependent dynamic meta-holography using a vanadium dioxide integrated metasurface[J]. Advanced Optical Materials, 2019, 7(12): 1900175.
[70] MILLER K J, HAGLUND R F, WEISS S M. Optical phase change materials in integrated silicon photonic devices: review[J]. Optical Materials Express, 2018, 8(8): 2415-2429.
[71] WANG J N, XIONG B, LIU Y, et al. Continuously and reversibly electro-tunable optical nanoantennas based on phase transition of vanadium dioxide[J]. New Journal of Physics, 2021, 23(7): 075002.
[72] SHU F Z, ZHANG L H, WANG J N, et al. Dynamically tunable bowtie nanoantennas based on the phase transition of vanadium dioxide[J]. Optics Letters, 2019, 44(11): 2752-2755.
[73] JIANG N, ZHUO X, WANG J. Active plasmonics: principles, structures and applications[J]. Chemical Reviews, 2018, 118(6): 3054-3099.
[74] LAIBLE F, GOLLMER D A, DICKREUTER S, et al. Continuous reversible tuning of the gap size and plasmonic coupling of bow tie nanoantennas on flexible substrates[J]. Nanoscale, 2018 10(31): 14915-14922.
[75] YANG Z, KO C, RAMANATHAN S. Oxide electronics utilizing ultrafast metal-insulator transitions[J]. Annual Review of Materials Research, 2011, 41: 337-367.
[76] LIU K, LEE S, YANG S, et al. Recent progresses on physics applications of vanadium dioxide[J]. Materials Today, 2018, 21(8): 875-896.
[77] SHI R, SHEN N, WANG J, et al. Recent advances in fabrication strategies, phase transition modulation, and advanced applications of vanadium dioxide[J]. Applied Physics Reviews, 2019, 6(1): 011312.
[78] CUEFF S, JOHN J, ZHANG Z, et al. VO_2 nanophotonics[J]. APL Photonics, 2020, 5(11): 110901.
[79] GONG Z, YANG F, WANG L, et al. Phase change materials in photonic devices[J]. Journal of Applied Physics, 2021, 129(3): 030902.
[80] WU C, FENG F, XIE Y. Design of vanadium oxide structures with controllable electrical properties for energy applications[J]. Chemical Society Reviews, 2013, 42(12): 5157-5183.
[81] PERGAMENT A L, STEFANOVICH G B, VELICHKO A A. Oxide electronics and vanadium dioxide perspective: a review[J]. IEEE Journal on Selected Topics in Nano Electronics and Computing, 2013, 1(1): 24-43.
[82] LIU M, SU B, TANG Y, et al. Recent advances in nanostructured vanadium oxides and composites for energy conversion [J]. Advanced Energy Materials, 2017, 7(23): 1700885.
[83] FERRARA D W, NAG J, MACQUARRIE E R, et al. Plasmonic probe of the semiconductor to metal phase transition in vanadium dioxide[J]. Nano Letters, 2013, 13(9): 4169-4175.
[84] KIM H T, CHAE B G, YOUN D H, et al. Raman study of electric-field-induced first-order metal-insulator transition in VO_2-based devices[J]. Applied Physics Letters, 2005, 86(24): 242101.
[85] LIU M, HWANG H Y, TAO H, et al. Terahertz-field-induced insulator-to-metal transition in vanadium dioxide metamaterial[J]. Nature, 2012, 487(7407): 345-348.
[86] MAIER S A. Plasmonics: fundamentals, applications[M]. New York: Springer, 2007.
[87] HALAS N J, LAL S, CHANG W S, et al. Plasmons in strongly coupled metallic nanostructures[J]. Chemical Reviews, 2011, 111(6): 3913-3961.
[88] LIU L, KANG L, MAYER T S, et al. Hybrid metamaterials for electrically triggered multifunctional control[J]. Nature Communications, 2016, 7: 13236.
[89] VERLEUR H W, BARKER A S, BERGLUND C N. Optical properties of VO_2 between 0.25 and 5 eV[J]. Physical Review, 1968, 172(3): 788-798.
[90] LIU K, CHENG C, CHENG Z, et al. Giant-amplitude, high-work density microactuators with phase transition activated nanolayer bimorphs[J]. Nano Letters, 2012, 12(12): 6302-6308.
[91] LIU K, CHENG C, SUH J, et al. Powerful, multifunctional torsional micromuscles activated by phase transition[J]. Advanced Materials, 2014, 26(11): 1746-1750.
[92] WANG T, TORRES D, FERNÁNDEZ F E, et al. Maximizing the performance of photothermal actuators by combining smart materials with supplementary advantages[J]. Science Advances, 2017, 3(4): e1602697.
[93] MA H, HOU J, WANG X, et al. Flexible, all-inorganic actuators based on vanadium dioxide and carbon nanotube

bimorphs[J]. Nano Letters, 2017, 17(1): 421-428.
[94] JEONG J, AETUKURI N, GRAF T, et al. Suppression of metal-insulator transition in VO_2 by electric field-induced oxygen vacancy formation[J]. Science, 2013, 339(6126): 1402-1405.
[95] WU C, ZHANG X, DAI J, et al. Direct hydrothermal synthesis of monoclinic VO_2(M) single-domain nanorods on large scale displaying magnetocaloric effect[J]. Journal of Materials Chemistry, 2011, 21(12): 4509-4517.
[96] KE Y, WANG S, LIU G, et al. Vanadium dioxide: the multistimuli responsive material and its applications[J]. Small, 2018, 14(39): 1802025.
[97] WAN C, ZHANG Z, WOOLF D, et al. On the optical properties of thin-film vanadium dioxide from the visible to the far infrared[J]. Annalen Der Physik, 2019, 531(10): 1900188.
[98] JOHN J, GUTIERREZ Y, ZHANG Z, et al. Multipolar resonances with designer tunability using VO_2 phase-change materials[J]. Physical Review Applied, 2020, 13(4): 044053.
[99] DRISCOLL T, KIM H T, CHAE B G, et al. Memory metamaterials[J]. Science, 2009, 325(5947): 1518-1521.
[100] HORMOZ S, RAMANATHAN S. Limits on vanadium oxide Mott metal-insulator transition field-effect transistors[J]. Solid-State Electronics, 2010, 54(6): 654-659.
[101] APPAVOO K, HAGLUND R F. Polarization selective phase-change nanomodulator[J]. Scientific Reports, 2014, 4: 6771.
[102] RYCKMAN J D, HALLMAN K A, MARVEL R E, et al. Ultra-compact silicon photonic devices reconfigured by an optically induced semiconductor-to-metal transition[J]. Optics Express, 2013, 21(9): 10753-10763.
[103] LI S Y, NIKLASSON G A, GRANQVIST C G. Thermochromic fenestration with VO_2-based materials: Three challenges and how they can be met[J]. Thin Solid Films, 2012, 520(10): 3823-3828.
[104] BRIGGS R M, PRYCE I M, ATWATER H A. Compact silicon photonic waveguide modulator based on the vanadium dioxide metal-insulator phase transition[J]. Optics Express, 2010, 18(11): 11192-11201.
[105] MARKOV P, MARVEL R E, CONLEY H J, et al. Optically monitored electrical switching in VO_2[J]. ACS Photonics, 2015, 2(8): 1175-1182.
[106] LI C, HU X, GAO W, et al. Thermo-optical tunable ultracompact chip-integrated 1D photonic topological insulator[J]. Advanced Optical Materials, 2018, 6(4): 1701071.
[107] RENSBERG J, ZHANG S, ZHOU Y, et al. Active optical metasurfaces based on defect-engineered phase-transition materials[J]. Nano Letters, 2016, 16(2): 1050-1055.
[108] MORIN F J. Oxides which show a metal-to-insulator transition at the Neel temperature[J]. Physical Review Letters, 1959, 3(1): 34-36.
[109] WEGKAMP D, STÄHLER J. Ultrafast dynamics during the photoinduced phase transition in VO_2[J]. Progress in Surface Science, 2015, 90(4): 464-502.
[110] GOODENOUGH J B. The two components of the crystallographic transition in VO_2[J]. Journal of Solid State Chemistry, 1971, 3(4): 490-500.
[111] MAREZIO M, MCWHAN D B, REMEIKA J P, et al. Structural aspects of the metal-insulator transitions in Cr-doped VO_2[J]. Physical Review B, 1972, 5(7): 2541-2551.
[112] WANG X, DONG K, CHOE H S, et al. Multifunctional microelectro-opto-mechanical platform based on phase-transition materials[J]. Nano Letters, 2018, 18(3): 1637-1643.
[113] AETUKURI N B, GRAY A X, DROUARD M, et al. Control of the metal-insulator transition in vanadium dioxide by modifying orbital occupancy[J]. Nature Physics, 2013, 9(10): 661-666.
[114] ZYLBERSZTEJN A, MOTT N F. Metal-insulator transition in vanadium dioxide[J]. Physical Review B, 1975, 11(11): 4383-4395.
[115] CAPELLO M, BECCA F, FABRIZIO M, et al. Variational description of Mott insulators[J]. Physical Review Letters, 2005, 94(2): 026406.
[116] TOMCZAK J M, ARYASETIAWAN F, BIERMANN S. Effective bandstructure in the insulating phase versus strong dynamical correlations in metallic VO_2[J]. Physical Review B, 2008, 78(11): 115103.
[117] LAZAROVITS B, KIM K, HAULE K, et al. Effects of strain on the electronic structure of VO_2[J]. Physical Review B, 2010, 81(11): 115117.
[118] WEBER C, O'REGAN D D, HINE N D M, et al. Vanadium dioxide: A Peierls-Mott insulator stable against disorder [J]. Physical Review Letters, 2012, 108(25): 256402.
[119] PARK J H, COY J M, KASIRGA T S, et al. Measurement of a solid-state triple point at the metal-insulator transition in VO_2[J]. Nature, 2013, 500(7463): 431-434.
[120] BUDAI J D, HONG J, MANLEY M E, et al. Metallization of vanadium dioxide driven by large phonon entropy[J]. Nature, 2014, 515(7528): 535-539.
[121] LEE S, HIPPALGAONKAR K, YANG F, et al. Anomalously low electronic thermal conductivity in metallic

vanadium dioxide[J]. Science, 2017, 355(6323): 371-374.
[122] LEE D, CHUNG B, SHI Y, et al. Isostructural metal-insulator transition in VO_2[J]. Science, 2018, 362(6418): 1037-1040.
[123] KAWATA S, INOUYE Y, VERMA P. Plasmonics for near-field nano-imaging and superlensing [J]. Nature Photonics, 2009, 3(7): 388-394.
[124] MARVEL R E, APPAVOO K, CHOI B K, et al. Electron-beam deposition of vanadium dioxide thin films[J]. Applied Physics A-Materials Science & Processing, 2013, 111(3): 975-981.
[125] QAZILBASH M M, BREHM M, CHAE B G, et al. Mott transition in VO_2 revealed by infrared spectroscopy and nano-imaging[J]. Science, 2007, 318(5857): 1750-1753.
[126] KATS M A, BLANCHARD R, ZHANG S, et al. Vanadium dioxide as a natural disordered metamaterial: perfect thermal emission and large broadband negative differential thermal emittance [J]. Physical Review X, 2013, 3(4): 041004.
[127] FIORINO A, THOMPSON D, ZHU L, et al. A thermal diode based on nanoscale thermal radiation[J]. ACS Nano, 2018, 12(6): 5774-5779.
[128] TANG K, WANG X, DONG K, et al. A thermal radiation modulation platform by emissivity engineering with graded metal - insulator transition[J]. Advanced Materials, 2020, 32(36): 1907071.
[129] KANA J B K, NDJAKA J M, VIGNAUD G, et al. Thermally tunable optical constants of vanadium dioxide thin films measured by spectroscopic ellipsometry[J]. Optics Communications, 2011, 284(3): 807-812.
[130] GAO Y, LUO H, ZHANG Z, et al. Nanoceramic VO_2 thermochromic smart glass: a review on progress in solution processing[J]. Nano Energy, 2012, 1(2): 221-246.
[131] LI S Y, NIKLASSON G A, GRANQVIST C G. Thermochromic fenestration with VO_2-based materials: three challenges and how they can be met[J]. Thin Solid Films, 2012, 520(10): 3823-3828.
[132] WAN C, HORAK E H, KING J, et al. Limiting optical diodes enabled by the phase transition of vanadium dioxide[J]. ACS Photonics 2018, 5(7): 2688-2692.
[133] STEFANOVICH G, PERGAMENT A, STEFANOVICH D. Electrical switching and Mott transition in VO_2[J]. Journal of Physics: Condensed Matter, 2000, 12(41): 8837-8845.
[134] KIM H T, CHAE B G, YOUN D H, et al. Mechanism and observation of Mott transition in VO_2-based two- and three-terminal devices[J]. New Journal of Physics, 2004, 6: 52.
[135] LEE M J, PARK Y, SUH D S, et al. Two series oxide resistors applicable to high speed and high density nonvolatile memory[J]. Advanced Materials, 2007, 19(22): 3919-3923.
[136] DRISCOLL T, KIM H T, CHAE B G, et al. Phase-transition driven memristive system[J]. Applied Physics Letters, 2009, 95(4): 043503.
[137] RUZMETOV D, GOPALAKRISHNAN G, KO C, et al. Three-terminal field effect devices utilizing thin film vanadium oxide as the channel layer[J]. Journal of Applied Physics, 2010, 107(11): 114516.
[138] NAKANO M, SHIBUYA K, OKUYAMA D, et al. Collective bulk carrier delocalization driven by electrostatic surface charge accumulation[J]. Nature, 2012, 487(7408): 459-462.
[139] YAJIMA T, NISHIMURA T, TORIUMI A. Positive-bias gate-controlled metal-insulator transition in ultrathin VO_2 channels with TiO2 gate dielectrics[J]. Nature Communications, 2015, 6: 10104.
[140] KUMAR S, PICKETT M D, STRACHAN J P, et al. Local temperature redistribution and structural transition during Joule-heating-driven conductance switching in VO_2[J]. Advanced Materials, 2013, 25(42): 6128-6132.
[141] ZIMMERS A, AIGOUY L, MORTIER M, et al. Role of thermal heating on the voltage induced insulator-metal transition in VO_2[J]. Physical Review Letters, 2013, 110(5): 056601.
[142] LI H, PENG H, JI C, et al. Electrically tunable mid-infrared antennas based on VO_2[J]. Journal of Modern Optics, 2018, 65(15): 1809-1816.
[143] ZHANG C, ZHOU G, WU J, et al. Active control of terahertz waves using vanadium-dioxide-embedded metamaterials [J]. Physical Review Applied, 2019, 11(5): 054016.
[144] CAVALLERI A, TÓTH CS, SIDERS C W, et al. Femtosecond structural dynamics in VO_2 during an ultrafast solid-solid phase transition[J]. Physical Review Letters, 2001, 87(23): 237401.
[145] KÜBLER C, EHRKE H, HUBER R, et al. Coherent structural dynamics and electronic correlations during an ultrafast insulator-to-metal phase transition in VO_2[J]. Physical Review Letters, 2007, 99(11): 116401.
[146] BAUM P, YANG D S, ZEWAIL A H. 4D visualization of transitional structures in phase transformations by electron diffraction[J]. Science, 2007, 318(5851): 788-792.
[147] TAO Z, HAN T T, MAHANTI S D, et al. Decoupling of structural and electronic phase transitions in VO_2[J]. Physical Review Letters, 2012, 109(16): 166406.
[148] MORRISON V R, CHATELAIN R P, TIWARI K L, et al. A photoinduced metal-like phase of monoclinic VO_2

revealed by ultrafast electron diffraction[J]. Science, 2014, 346(6208): 445-448.
[149] APPAVOO K, WANG B, BRADY N F, et al. Ultrafast phase transition via catastrophic phonon collapse driven by plasmonic hot-electron injection[J]. Nano Letters, 2014, 14(3): 1127-1133.
[150] WALL S, YANG S, VIDAS L, et al. Ultrafast disordering of vanadium dimers in photoexcited VO_2[J]. Science, 2018, 362(6414): 572-576.
[151] FAN R H, ZHU L H, PENG R W, et al. Broadband antireflection and light-trapping enhancement of plasmonic solar cells[J]. Physical Review B, 2013, 87(19): 195444.
[152] SHI W B, LIU L Z, PENG R W, et al. Strong localization of surface plasmon polaritons with engineered disorder[J]. Nano Letters, 2018, 18(3): 1896-1902.
[153] ZHU Y Y, JING H, PENG R W, et al. Realizing Anderson localization of surface plasmon polaritons and enhancing their interactions with excitons in 2D disordered nanostructures[J]. Applied Physics Letters, 2020, 116(20): 201106.
[154] SUH J Y, DONEV E U, LOPEZ R, et al. Modulated optical transmission of subwavelength hole arrays in metal- VO_2 films[J]. Applied Physics Letters, 2006, 88(13): 133115.
[155] KATS M A, BLANCHARD R, GENEVET P, et al. Thermal tuning of mid-infrared plasmonic antenna arrays using a phase change material[J]. Optics Letters, 2013, 38(3): 368-370.
[156] EARL S K, JAMES T D, DAVIS T J, et al. Tunable optical antennas enabled by the phase transition in vanadium dioxide[J]. Optics Express, 2013, 21(22): 27503-27508.
[157] MATSUI H, HO Y L, KANKI T, et al. Mid-infrared plasmonic resonances in 2D VO_2 nanosquare arrays[J]. Advanced Optical Materials, 2015, 3(12): 1759-1767.
[158] MUSKENS O L, BERGAMINI L, WANG Y, et al. Antenna-assisted picosecond control of nanoscale phase transition in vanadium dioxide[J]. Light: Science & Applications, 2016, 5: e16173.
[159] KIM S J, YUN H, PARK K, et al. Active directional switching of surface plasmon polaritons using a phase transition material[J]. Scientific Reports, 2017, 7: 43723.
[160] KE Y, WEN X, ZHAO D, et al. Controllable fabrication of two-dimensional patterned VO_2 nanoparticle, nanodome, and nanonet arrays with tunable temperature-dependent localized surface plasmon resonance[J]. ACS Nano, 2017, 11(7): 7542-7551.
[161] HAO Q, LI W, XU H, et al. VO_2/TiN plasmonic thermochromic smart coatings for room-temperature applications[J]. Advanced Materials, 2018, 30(10): 1705421.
[162] NAGASAKI Y, KOHNO T, BANDO K, et al. Adaptive printing using VO_2 optical antennas with subwavelength resolution[J]. Applied Physics Letters, 2019, 115(16): 161105.
[163] XIONG X, XUE Z H, MENG C, et al. Polarization-dependent perfect absorbers/reflectors based on a three-dimensional metamaterial[J]. Physical Review B, 2013, 88(11): 115105.
[164] XIONG X, JIANG S C, HU Y H, et al. Structured metal film as a perfect absorber[J]. Advanced Materials, 2013, 25(29): 3994-4000.
[165] XIONG X, HU Y S, JIANG S C, et al. Metallic stereostructured layer: An approach for broadband polarization state manipulation[J]. Applied Physics Letters, 2014, 105(20):201105.
[166] DICKEN M J, AYDIN K, PRYCE I M, et al. Frequency tunable near-infrared metamaterials based on VO_2 phase transition[J]. Optics Express, 2009, 17(20): 18330-18339.
[167] HUANG W X, YIN X G, HUANG C P, et al. Optical switching of a metamaterial by temperature controlling[J]. Applied Physics Letters, 2010, 96(26): 261908.
[168] APPAVOO K, HAGLUND R F. Detecting nanoscale size dependence in VO_2 phase transition using a split-ring resonator metamaterial[J]. Nano Letters, 2011, 11(3): 1025-1031.
[169] KRISHNAMOORTHY H N S, ZHOU Y, RAMANATHAN S, et al. Tunable hyperbolic metamaterials utilizing phase change heterostructures[J]. Applied Physics Letters, 2014, 104(12): 121101.
[170] HASHEMI M R M, YANG S H, WANG T, et al. Electronically-controlled beam-steering through vanadium dioxide metasurfaces[J]. Scientific Reports, 2016, 6: 35439.
[171] ZHU Z, EVANS P G, HAGLUND R F, et al. Dynamically reconfigurable metadevice employing nanostructured phase-change materials[J]. Nano Letters, 2017, 17(8): 4881-4885.
[172] SUN K, RIEDEL C A, URBANI A, et al. VO_2 thermochromic metamaterial-based smart optical solar reflector[J]. ACS Photonics 2018, 5(6): 2280-2286.
[173] SONG Z, WANG K, LI J, et al. Broadband tunable terahertz absorber based on vanadium dioxide metamaterials[J]. Optics Express, 2018, 26(6): 7148-7154.
[174] PARK D J, SHIN J H, PARK K H, et al. Electrically controllable THz asymmetric split-loop resonator with an outer square loop based on VO_2[J]. Optics Express, 2018, 26(13): 17397-17406.
[175] ZHAO Y, ZHANG Y, SHI Q, et al. Dynamic photoinduced controlling of the large phase shift of terahertz waves via

vanadium dioxide coupling nanostructures[J]. ACS Photonics 2018, 5(8): 3040-3050.
[176] LIU M, PLUM E, LI H, et al. Temperature-controlled optical activity and negative refractive index[J]. Advanced Functional Materials, 2021, 31(14): 2010249.
[177] WAN C, ZHANG Z, SALMAN J, et al. Ultrathin broadband reflective optical limiter[J]. Laser Photonics Reviews, 2021, 15(6): 2100001.
[178] JIANG S C, XIONG X, SARRIUGARTE P, et al. Tuning the polarization state of light via time retardation with a microstructured surface[J]. Physical Review B, 2013, 88(16): 161104.
[179] GAO Y J, WANG Z Y, TANG W J, et al. Metasurface design for the generation of an arbitrary assembly of different polarization state[J]. Physical Review B, 2021, 104(12): 125419.
[180] CHU H C, ZHANG H Y, ZHANG Y, et al. Invisible surfaces enabled by the coalescence of anti-reflection and wavefront controllability in ultrathin metasurfaces[J]. Nature Communications, 2021, 12(1): 4523.
[181] CHU H C, XIONG X, GAO Y J, et al. Diffuse reflection and reciprocity-protected transmission via a random-flip metasurface[J]. Science Advances, 2021, 7(37): eabj0935.
[182] DING F, ZHONG S, BOZHEVOLNYI S I, et al. Vanadium dioxide integrated metasurfaces with switchable functionalities at terahertz frequencies[J]. Advanced Optical Materials, 2018, 6(9): 1701204.
[183] CAI H, CHEN S, ZOU C, et al. Multifunctional hybrid metasurfaces for dynamic tuning of terahertz waves[J]. Advanced Optical Materials, 2018, 6(14): 1800257.
[184] NOUMAN M T, HWANG J H, FAIYAZ M, et al. Vanadium dioxide based frequency tunable metasurface filters for realizing reconfigurable terahertz optical phase and polarization control[J]. Optics Express, 2018, 26(10): 12922-12929.
[185] BUTAKOV N A, VALMIANSKI I, LEWI T, et al. Switchable plasmonic-dielectric resonators with metal-insulator transitions[J]. ACS Photonics, 2018, 5(2): 371-377.
[186] DONG K, HONG S, DENG Y, et al. A lithography-free and field-programmable photonic metacanvas[J]. Advanced Materials, 2018, 30(5): 1703878.
[187] KIM Y, WU P C, SOKHOYAN R, et al. Phase modulation with electrically tunable vanadium dioxide phase-change metasurfaces[J]. Nano Letters, 2019, 19(6): 3961-3968.
[188] KARGAR R, ROUHI K, ABDOLALI A. Reprogrammable multifocal THz metalens based on metal - insulator transition of VO_2-assisted digital metasurface[J]. Optics Communications, 2020, 462: 125331.
[189] LIU M, PLUM E, LI H, et al. Switchable chiral mirrors[J]. Advanced Optical Materials, 2020, 8(15): 2000247.
[190] HOWES A, ZHU Z, CURIE D, et al. Optical limiting based on Huygens' metasurfaces[J]. Nano Letters, 2020, 20(6): 4638-4644.
[191] HU Y, TONG M, XU Z, et al. Spatiotemporal terahertz metasurfaces for ultrafast all-optical switching with electric-triggered bistability[J]. Laser Photonics Reviews, 2021, 15(3): 2000456.
[192] KEPIČ P, LIGMAJER F, HRTOŇ M, et al. Optically tunable Mie resonance VO_2 nanoantennas for metasurfaces in the visible[J]. ACS Photonics, 2021, 8(4): 1048-1057.
[193] TRIPATHI A, JOHN J, KRUK S, et al. Tunable Mie-resonant dielectric metasurfaces based on VO_2 phase-transition materials[J]. ACS Photonics, 2021, 8(4): 1206-1213.
[194] WEI H, WANG Z, TIAN X, et al. Cascaded logic gates in nanophotonic plasmon networks[J]. Nature Communications, 2011, 2: 387.
[195] HU Q, ZHAO J Z, PENG R W, et al. "Rainbow" trapped in a self-similar coaxial optical waveguide[J]. Applied Physics Letters, 2010, 96(16): 161101.
[196] HU Q, XU D H, ZHOU Y, et al. Position-sensitive spectral splitting with a plasmonic nanowire on silicon chip[J]. Scientific Reports, 2013, 3: 3095.
[197] HU Q, XU D H, PENG R W, et al. Tune the "rainbow" trapped in a multilayered waveguide[J]. Europhysics Letters, 2012, 99(5): 57007.
[198] CAI J, CHEN B, WU J, et al. Reconfigurable terahertz rainbow deflector[J]. Applied Physics Letters, 2021, 118(14): 141105.

Dynamically Tunable Optical Materials and Devices Based on Phase Transition of Vanadium Dioxide (Invited)

FAN Renhao, HOU Benqi, PENG Ruwen, WANG Mu

(*National Laboratory of Solid State Microstructures and School of Physics, Nanjing University, Nanjing* 210093, *China*)

Abstract: Artificially subwavelength metastructures, such as metamaterials and metasurfaces, can realize novel optical properties that natural materials do not possess and manipulate electromagnetic waves. However, optical materials and devices based on static structures often only have fixed optical functions, which are challenging to deal with complex and changeable application requirements. In recent years, phase change materials such as vanadium dioxide have been introduced into artificial metastructures, realizing a series of tunable optical materials and devices that can dynamically change the functionalities and gain real-time control. This paper reviews recent advances in dynamically tunable optical materials and devices based on the phase transition of vanadium dioxide as following:

Firstly, we introduce the research on vanadium dioxide′s structure, phase transition mechanism, and physical properties. Vanadium dioxide undergoes an insulator-metal phase transition when heated to about 68℃, and its crystal structure convert from a monoclinic insulator structure to a rutile metal structure. Based on its crystal structure, the Young's modulus of vanadium dioxide is about 140 GPa, the strain is about 1%, and its mechanical work output per unit volume is as high as 7 J/cm^3, so vanadium dioxide is suitable for deformable materials or actuator materials. Since the crystal structure of vanadium dioxide changes after the phase transition, its corresponding energy band structure also changes accordingly. Based on the conversion in the crystal structure and energy band structure of vanadium dioxide before and after the phase transition, people have been working to explore the physical mechanism of its phase transition. Although vanadium dioxide has been studied for more than 60 years, its phase transition mechanism has been controversial for a long time. Two theories have long existed for the phase transition mechanism of vanadium dioxide: the first is the Peierls transition caused by lattice distortion; the second is the Mott transition caused by electron correlation. Recent theoretical treatments tend to bridge the gap between the purely Mott-like and purely Peierls-like pictures.

Secondly, the phase transition of vanadium dioxide that can be tuned by external excitations such as heat, electricity, and light have been introduced. The refractive index, dielectric function, and resistance of vanadium dioxide before and after the phase transition and during the phase transition undergo reversible and significant changes. This feature makes it possible to dynamically tune the electromagnetic waves. Various external stimulus has been found to excite the phase transition of vanadium dioxide, such as temperature, optical field, electric field, electrical current, magnetic field, electrochemistry and stress. Among them, thermally, electrically or optically tuning phase transitions of vanadium dioxide are suitable for the design of dynamic optical materials and devices, and have been widely used. Therefore, three excitation methods to make phase transition of vanadium dioxide are introduced here.

Thirdly, we summarize recent progress on active materials, structures, and devices based on phase transition of vanadium dioxide, including active metamaterials, metasurfaces, plasmonic nanostructures and waveguides. Integrating vanadium dioxide into optical materials and devices endows those based on static artificial micro-nano structures post-fabrication tunablity. So that dynamically tunable optical materials and devices based on vanadium dioxide phase transition can cope with complex and changeable application scenarios and practical requirements for device versatility.

Finally, a brief summary and outlook are given. We expect that this article promotes the development of novel active materials and devices in optoelectronics.

Key words: Metamaterials; Plasmonics; Dynamical tuning; Phase transition of vanadium dioxide; Metasurfaces

OCIS Codes: 160.3918; 160.4670; 230.3990; 250.5403

Foundation item: National Natural Science Foundation of China (Nos. 11634005, 61975078, 11974177), National Key Research and Development Program of China (No. 2017YFA0303702)