Recent Progress in Active Optical Metasurfaces

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Abstract:
Evolving from metamaterials, optical metasurfaces not only inherit their unprecedented flexibility in tailoring light–matter interaction but also the generally fixed response determined by the meta-atoms’ geometries — an undesirable property that hinders the development of practical metadevices. Consequently, novel optical metasurfaces that can be tuned in an active manner have been intensively studied in recent years. Due to their optically thin structures, optical metasurfaces present unique characteristics in the realization of dynamic tuning. In this review, a detailed summary of the recent advances in active optical metasurfaces is provided including discussions reviewing a variety of active materials and approaches that enable faster, stronger and more accurate tuning. Beyond facilitating practical metadevices, studies of active metasurfaces have, and will continue to deepen our understandings of the interaction between light and nanostructured photonic architectures and to promote the development of nanofabrication techniques involving high-complexity.

Keywords: optical metasurfaces, tunable devices, reconfigurable devices, metadevices

1. Introduction

The application of artificial structures in optics has a long history, while the use of those constructed by subwavelength building blocks is a recent development. As an example, the Fresnel lens was originally created to reduce the thickness and weight of conventional lenses by dividing the lens into a set of macroscopic concentric annular sections. Structures with subwavelength features that enhance the light–matter interaction, which were firstly used in the RF regime, have only been extended to optical frequencies over the past few decades because of recent advances in nano-
fabrication techniques. Their introduction can be traced to the mid-1980s when the photonic crystal work by Yablonovitch and John began to attract great interest.\textsuperscript{[1,2]} Indeed, based on the periodic variation of its dielectric constant, photonic crystals may be engineered to manipulate the propagation, strong localization, spontaneous emission, etc. of light in specified frequency bands. The explosive development of metamaterials over the past decade or more has provided new inroads in this field. Specifically, the concept of meta-atoms has enabled unprecedented flexibility in tailoring effective material parameters at optical frequencies. Moreover, by exploiting surface plasmon polaritons (SPPs), photonic metamaterials have enabled the engineering of light-matter interactions on subwavelength scales. A series of interesting optical phenomena including negative refraction,\textsuperscript{[3]} optical magnetism,\textsuperscript{[4,5]} giant optical chirality,\textsuperscript{[6]} hyperlens effect,\textsuperscript{[7,8]} etc. have been discovered through nanostructure-based designs. The field of photonic metamaterials is growing but continues to face two main challenges: (1) The high Ohmic loss in the optical regime due to increased electron scattering at metal surfaces which can lead to dysfunction of the photonic metadevices, and (2) the difficulty of fabricating the required deep-subwavelength features of the meta-atoms whose structure may be highly complex.

In sharp contrast to the approach of designing metamaterials with responses determined by their bulk effective optical properties, optical metasurfaces, a newly emerging field of nano-optics, gain their properties from single-layer or few-layer planar artificial structures. Accordingly, the metasurface-based manipulation of optical waves may in general only involve interaction between light and planar architectures with subwavelength thickness, which results in largely reduced optical loss and simultaneously allows engineers to circumvent the difficulty encountered in fabricating three-dimensional (3D) photonic metamaterials. These advantages not only provide an enormous opportunity for designing practical photonic metadevices, but also make metasurfaces a novel platform for the exploration of surface-plasmon directed light-matter interaction on a nanometer scale. In particular, owing to their ability to manipulate fundamental properties of optical waves, including phase, amplitude, polarization, angular momentum, etc., metasurfaces have been used to demonstrate a series of intriguing phenomena. These include such effects as anomalous reflection and refraction,\textsuperscript{[9,10]} photonic spin hall effect,\textsuperscript{[11]} vortex-beam generation,\textsuperscript{[9,12]} helicity-controlled SPPs coupling,\textsuperscript{[13,14]} invisibility skin cloak,\textsuperscript{[15]} metalensing effects at visible wavelengths,\textsuperscript{[16]} to name a few. In addition, the integration of photonic metasurfaces and natural material systems, such as two-dimensional (2D) materials (e.g. graphene\textsuperscript{[17,18]} and WS\textsubscript{2}\textsuperscript{[19]}), quantum dots,\textsuperscript{[20,21]} phonon systems,\textsuperscript{[22,23]} phase change materials,\textsuperscript{[24,25]} offers a unique approach to investigate the coupling between nanoplasmonic resonators and various types of emerging materials by harnessing the plasmonic resonances resulting from field enhancement and dispersion engineering flexibility.
Considering the power and versatility of metasurfaces, it is not surprising that they have attracted widespread interest in recent years. However, given the fact that metasurfaces derive their properties from plasmonic resonance as well as the geometric arrangement of meta-atoms, their responses are generally fixed and cannot be dynamically altered — an issue that has received a good deal of attention. In other words, tunability and reconfigurability are dominant factors for designing metadevices with practical functionalities. To this end, researchers have been leveraging the capabilities discussed above and redirecting them for the creation of nanoarchitectures that can actively respond to external stimuli. Consequently, in parallel to the studies of various types of exotic optical phenomena enabled by metasurfaces, efforts are also being made to develop novel optical metasurfaces that are both dynamic and reversibly tunable. It should be noted that beyond the linear regime, optical metasurfaces have also been exploited to control the energy, polarization, and phase of light in the nonlinear regime through the design of subwavelength meta-atoms. A number of studies have been performed to explore a variety of fundamental phenomena of nonlinear metasurfaces, such as the nonlinear generation selectivity, nonlinear phase and wavefront modulation, ultrafast response, etc. Given the importance and rapid development of nonlinear metasurfaces, a few review papers that are dedicated to different aspects of nonlinearity in metasurfaces have recently been published.

A close inspection of the dynamically tunable metasurfaces reveals that two primary strategies can be employed to achieve active responses: (i) hybridizing metals and active media possessing variable refractive indices whereby the active media regulates plasmonic resonances arising from the metallic nanostructures, and (ii) creating metasurfaces directly using building blocks made of active materials. In addition, varying the physical structure is another important means of achieving tunability, as seen in mechanically tunable metasurfaces. Although previous research on tunable metamaterials provides a major source of inspiration, the realization of dynamic optical metasurfaces comes with its own set of unique features and design challenges. First, the plasmonic response in optical metasurfaces, attributed to the interaction between light and optically thin structures, can be modulated relatively easily by controlling the optical properties of materials in proximity to the meta-atoms’ surfaces. This not only eases the hybridization between plasmonic resonators and active media, such as phase change materials (e.g. vanadium dioxide (VO$_2$)) and transparent conducting oxides (e.g. indium tin oxide (ITO)) in the form of thin films, but also allows the exploration of large response modulation enabled by 2D materials (e.g. graphene) that are only a single atomic layer thick. Second, requiring only simple planar structures, optical metasurfaces open up the possibility of active photonics using dielectric (e.g. silicon (Si)) resonators as frequency-agile nanoantennas owing to their low-loss characteristics and tunable Mie resonances under excitations.
Third, for ultra-fast modulation, the ultra-thin feature of optical metasurfaces can significantly improve their transient response to external excitations (such as laser pumping), leading to temporal processes much less dependent on undesired thermo-optical effects that correspond to plasmonic heating and slow thermal dissipation. Besides these, the structural characteristics of optical metasurfaces also suggest the possibility for other unique tuning mechanisms which were unsuitable or impossible for bulk metamaterial systems. For instance, nanochemistry enabled active responses have been observed in metal nanocavity structures that simultaneously support infrared optical resonances and nanofluidic functionality,\cite{40} while chemical reaction in magnesium (Mg) nanostructures involving hydrogenation/dehydrogenation processes have been used to realize plasmonic resonance tuning in the visible regime.\cite{41,42}

Owing to the rapid advances of this field which are of interest to researchers in various disciplines, we have chosen to focus this Progress Report primarily on the most recent development of active optical metasurfaces in the linear regime, while occasionally addressing their nonlinearity. In order to present the tunability offered by various materials and methods, we organize the major part of this paper as follows. In Section 2, 3, 4 and 5, we will discuss the response tuning of optical metasurfaces based on phase change materials (GST and VO\textsubscript{2}), ITO, graphene and liquid crystals respectively. Discussion on the topic of reconfigurable dielectric metasurfaces will be included in Section 6. Mechanical tunability will be discussed in Section 7, while other interesting tuning materials and methods will be addressed in Section 8. Finally in Section 9, conclusions and a scope for future research are provided.

2. Phase Change Materials

2.1 Germanium-Antimony-Tellurium (GST)

As the most commercialized phase-change material, GeSbTe (germanium-antimony-tellurium or GST) is commonly employed as the active material in information storage devices such as rewritable optical discs and memory devices. In brief, GST can switch between an amorphous (glass) state and a crystalline state and accordingly show significant change in both real (Re\(n\)) and imaginary (Im\(n\)) parts of refractive index as well as other electrical properties. GST has a crystallization temperature of around 150 °C and melting point about 600 °C. For conventional rewritable optical discs, a low-intensity laser beam is first used to crystallize the GST by heating it up to a temperature between 150 and 600 °C. After a brief cooling process, high-intensity nanosecond laser pulses are used to write information by heating the same spot beyond the melting temperature and leaving GST in its amorphous state. Since the phase change behavior of GST originates from its alloy nature, its
melting point and glass transition temperature can be varied by controlling stoichiometry of the ternary compound. Owing to these flexibilities in the material properties, GST has attracted great attention as an active medium for the construction of reconfigurable optical metadevices.

2.1.1 GST-hybrid metasurfaces

Despite the fact that phase changes generally lead to variation of material properties in a broad frequency band, GST is nevertheless attractive for creating hybrid mid-infrared (Mid-IR) metasurfaces due to its low-loss and larger structural-transition enabled index change in the same region. Compared with other phase change materials, the well-established technique of GST fabrication is already amenable to hybridization due to the high quality GST thin films which can currently be obtained through magnetron sputtering using argon as the sputtering gas. Although optically triggered phase transition was reported in an early study, tuning of GST-hybrid metasurfaces has been primarily achieved through direct thermal control. In particular, the large change in refractive index of GST has been used to tune a variety of metasurface properties, including nanoantenna resonance characteristics, absorption/emission properties, chirality and phase discontinuities among others.

Previous and recent studies on GST-hybrid nanoantennas systems revealed that through the control of GST’s different intermediate phases, the optical properties (such as transmission and reflection coefficients) of the hybrid systems can be precisely tuned within the range determined by the refractive index of GST in the amorphous and crystalline states. Beyond enabling these relatively straightforward nanoantennas’ tuning, GST has been used recently in more complicated systems for specific functionalities. GST based switchable geometric phase coded metasurfaces have been recently reported. Phase discontinuity in geometric metasurfaces arises from the in-plane relative rotation of meta-atoms that allows the impressing of the corresponding geometric phase on the cross-polarized fraction of an incident circularly polarized (CP) wave. Due to its dispersionless (broadband) behavior, geometric phase has attracted great attention as an alternative method for wavefront manipulation. As illustrated in the inset of Figure 1a, Yin et al. optimized nanorods A and B to resonate at a wavelength around 3.2 μm when GST is in its amorphous and crystalline states, respectively, and then arranged the two sets of nanoantennas to be clockwise and counter-clockwise rotated. Consequently, the hybrid metasurface selectively picks up geometric phase provided by nanoantennas A and B and exhibits transmitted beam switching when the phase transition occurs. By arranging nanoantenna A and B into different gradient phase distributions, a cylindrical bifocal lens was further demonstrated based on the same concept. Additionally, Yin et al. identified chiral response tuning, particularly the handedness switching of a
GST-hybrid plasmonic chiral metasurface.\cite{47} Experiments showed that amorphous-to-crystalline transition of GST326 inserted in the Born–Kuhn type resonators leads to a dramatic chiroptical spectra redshift of the hybrid chiral system. As illustrated in Figure 1b, Yin et al. then further demonstrated that handedness switching can be achieved through the use of delicately designed meta-molecules involving an active right-handed chiral resonator and another cascaded left-handed passive chiral resonator exhibiting weaker chiral resonance. Photonic chiral metasurfaces demonstrate a chiroptical response orders of magnitude higher than those observed in natural media,\cite{54–58} while reconfigurability may enhance their potential for ultracompact photonic polarization components,\cite{59–61} plasmonic-enhanced biological and chemical sensors,\cite{62} etc. Moreover, GST-hybrid metasurfaces recently have been used to demonstrate dynamic thermal emission control.\cite{50} Metamaterial/metasurface based absorbers are one of the most intriguing applications of metadevices to date. According to Kirchhoff’s law which states that at equilibrium the absorptivity of a material equals its emissivity, infrared metasurface absorbers may also be employed as thermal emitters with structure-determined emission properties. It was previously shown that the emissivity of the GST-hybrid metasurface absorber is closely dependent on the phase transition of GST.\cite{46} Cao et al. recently studied the dynamic control of multispectral thermal emission from a GST based ultrathin metasurface (Figure 1c).\cite{50} In this work, using the measured thermally tunable emissivity spectra, the authors developed a heat-transfer model revealing that reversible emission switching of the metasurfaces can occur in hundreds of nanoseconds.
Figure 1. Active metasurfaces based on phase transition of GST. (a) GST based geometric phase coded metasurfaces for beam switching. The SEM image shows a metasurface integrating two types of nanoantennas with distinct geometries into a supercell (top). Measured transmittance spectra when GST undergoes amorphous-to-crystalline transition (middle) and beam switching behavior indicated by infrared images and intensity plots (bottom) are also shown. Reproduced with permission. Copyright [year, publisher]. (b) Switchable chirality. Since the phase transition of GST redshifts the resonance of the active resonators, the handedness at the original resonance wavelength is determined by the passive resonators and experiences a sign switch. Reproduced with permission. Copyright [year, publisher]. (c) Reconfigurable phase-change metasurface thermal emitter. Reproduced with permission. Copyright [year, publisher].

2.1.2 GST structures based metasurfaces

A close inspection shows that in the infrared region GST possesses high refractive index in both the crystalline and amorphous phases (for instance, Re(ε_{c-GST@5 μm}) ~ 40 and Re(ε_{am-GST@5 μm}) ~ 11), which suggests that GST nanostructures should be able to support strong resonances that are closely dependent on its material phase. Consequently, phase control may lead to largely tunable optical responses of GST nanostructures even in the absence of metallic resonators. Based on this understanding, Werner et al. proposed and recently demonstrated a reconfigurable metasurface made of GST225 in the infrared. To achieve the maximum response tuning, genetic algorithm (GA) optimization was performed to create a pixelated pattern in the GST layer deposited on the fused silica substrate. In particular, as illustrated in Figure 2a, the GST layer in a unit cell was subdivided into an 8 × 8 grid of pixels and, using 8-fold symmetry, was represented by 10 unique binary bits. The encoding for a single triangle in the 8-fold symmetric unit cell is “0011,
where “0” represents a “No GST” pixel and “1” represents a “GST” pixel. Furthermore, a
Cost function in the GA was defined as $Cost = -dB(T_{am}) - dB\{\sqrt{1 - R_{cr}} - T_{cr}\}$, where the $T$ and
$R$ denote transmittance and reflectance for the amorphous ($\alpha$) and fcc crystalline ($cr$) phases
respectively. It was used to evaluate the overall performance of the metasurfaces. Measured
reflectance and transmittance of the optimized GST nanostructures revealed a phase transition
enabled modulation contrast as large as 7:1.

Harnessing the non-volatile amorphous-crystalline transitions in GST, researches have
previously demonstrated a series of interesting phenomena, including optical switching,[66] an
optically re-writable lensing effect,[67] and tunable beam steering[68] in GST nanostructure
metasurfaces. Compared with direct nanopatterning of GST films[66], a non-structured thin-film
design along with the ZnS–SiO2 protective layers[69] allows pulsed laser induced reversible
amorphous-crystalline transition in GST. This eliminates the potential physical and chemical issues in
the direct thermal triggering process.[66] Moreover, by controlling the number of laser pulses in a
certain range, different degrees of crystallization of the GST film can be achieved locally. These two
features have allowed for the generation of optical properties which are defined by erasable and
rewritable two-dimensional binary or greyscale patterns in nanoscale GST films, which has been
used to demonstrate a series of proof-of-concept reconfigurable devices, including bichromatic and
multi-focus Fresnel zone plates, a super-oscillatory lens, etc.[69] The structural phase transition of GST
was also employed as a changeable dielectric environment to manipulate the surface phonon–
polaritons (SPhPs) in quartz. Enabling strong light–matter interaction in the infrared region, SPhPs
are found on the surface of polar crystals due to collective photon-phonon coupling, although these
are challenging to manipulate because the lattice vibrations are primarily determined by the crystal
structures. By optically triggering the amorphous-to-crystalline transition of GST, Li et al.
demonstrated that the SPhPs switching in quartz can be achieved in a non-volatile and reversible
manner.[23] This showed that the properties of the SPhPs at air/GST/quartz interfaces like
confinement and dispersion are closely dependent on the thickness as well as material phase of the
GST thin film. Moreover, the propagation of SPhPs can be controlled through micrometer-scale
crystalline domains that are locally created by using nanosecond laser pulses in amorphous GST films
on quartz.
Besides the large index change in the near- and mid-infrared regions, recent studies have shown that delicately designed GST nanostructures can be used to realize sophisticated functionalities at shorter wavelengths because of GST’s switchable plasmonic response in the UV/visible range. Sreekanth et al. investigated the tunable absorption and phase singularity at visible wavelengths from a GST based asymmetric Fabry–Pérot (FP) cavity system. By fabricating a GST/silver multilayered nanocomposite structure, Krishnamoorthy et al. created type-I hyperbolic metamaterials (i.e., \( \text{Re}(\varepsilon_{\text{eff},\perp}) < 0, \text{Re}(\varepsilon_{\text{eff},/}) > 0 \)) exhibiting an effective permittivity that varies dramatically during the phase transition. When GST is in its amorphous state, the system satisfies the condition of \( \text{Re}(\varepsilon_{\text{eff},\perp}) < 0, \text{Re}(\varepsilon_{\text{eff},/}) > 0 \) in the entire wavelength range of interest while with crystalline GST the nanostructure may only behave as a type-I hyperbolic medium at wavelengths below ~770 nm. As a result, for a wavelength in the near-infrared (e.g., 1200 nm), triggering amorphous-to-crystalline transition of GST switches the refraction at the interface of the system from negative to positive and simultaneously enables negative refraction at a wavelength of, for example, 600 nm (Figure 2b). The controllable plasmonic response of GST has also been directly utilized to facilitate tunable responses of GST nanostructures in the visible region. Exploiting the
material property of GST at wavelength below 660 nm, i.e., where \( \text{Re}(\varepsilon_{\text{cr-GST}}) < 0 \) and \( \text{Re}(\varepsilon_{\text{am-GST}}) > 0 \), Gholipour et al. demonstrated a GST nanograting metasurface that exhibits switchable reflection/transmission behavior accompanied with remarkable color changes (Figure 2c), showing the potential of the proposed metasurface for active solid-state displays.\(^{[71]}\) The non-volatile phase transition properties of GST films can be applied to realize controllable mid-infrared thermal emission.\(^{[72,75]}\) It should be noted that contrary to the emissivity tuning of the GST-hybrid,\(^{[50]}\) the modulation addressed in these studies arises from the intrinsic emission change of the GST structures. For instance, a near-perfect thermal camouflage effect of a simple GST-Au layered structure was observed in background temperatures ranging from 30 °C to 50 °C (Figure 2d).\(^{[72]}\) Accordingly, the metasurfaces with a top layer of patterned GST can be spatially encoded and consequently decoded using a thermal camera. Du et al. recently reported GST-Al bilayer and Cr-GST-Au trilayer structures as wavelength-tunable mid-infrared thermal emitters.\(^{[75]}\) Importantly, using measured material properties of GST,\(^{[76]}\) the authors studied the absorption evolution of the two structures as a function of the degrees of crystallization of GST, which facilitates the continuously tunable emissivity of the proposed devices undergoing different annealing processes.

Based on the above discussion, we conclude that GST is suitable for enabling reconfigurability in various frequency bands, including the GST-hybrid metasurfaces and high-index GST nanostructures for mid-IR applications and, those based on plasmonic properties of GST at visible wavelengths. We also note that as the optical properties of GST are closely dependent on the material stoichiometry, the operating bands of GST metasurfaces may vary and so corresponding studies are desired.

2.2 Vanadium Dioxide (VO\(_2\))

2.2.1 VO\(_2\)-hybrid metasurfaces

Another phase change material vanadium dioxide (VO\(_2\)) has also attracted great attention as a promising candidate for reconfigurable metasurfaces. As a classical transition metal oxide, VO\(_2\) exhibits insulator-to-metal transition (IMT) around room temperature (\( T_{\text{IMT}} \approx 67 \) °C in bulk crystals) and consequently shows variations in the refractive index over a broad spectral range. The large variation in the material properties arises from the change in the crystal structure of VO\(_2\). Specifically, VO\(_2\) has a monoclinic lattice with the electrons localized in the atomic bonds at low temperature (insulator phase) and, at the transition temperature it experiences an atomic lattice rearrangement to a tetragonal structure that leads to strong lattice vibrations and the corresponding mobile electrons (metallic phase). Besides thermal excitation, the IMT of VO\(_2\) can also be triggered
by a variety of mechanisms, including optical pumping,\cite{77} charge injection\cite{78} and electrical signals,\cite{79} etc. Together, these properties make VO$_2$ highly attractive for low-power consuming and ultrafast tunable photonic metasurfaces. Dicken et al. were the first to demonstrate VO$_2$ phase transition enabled tunable metasurfaces in the near-infrared region,\cite{80} in which SRR-based planar resonators were fabricated on top of a VO$_2$ film and temperature dependent reflection spectra were experimentally observed. Kats et al. have shown that the mid-infrared plasmonic response of nanoantenna arrays can be modulated by using the index change of an underlying VO$_2$ substrate in proximity to its phase transition.\cite{81} Recent studies showed that, via direct thermal control, dynamically manipulated plasmonic color,\cite{82,83} extinction ratio\cite{84} and polarization state of light\cite{85} can be achieved in hybrid metasurfaces integrated with VO$_2$ nanostructures.

Figure 3. Tunable VO$_2$-hybrid metasurfaces based on thermally triggered IMT of VO$_2$. (a) Temperature dependent plasmonic color observed in arrays of silver nanodisks on VO$_2$ films. Reproduced with permission.\cite{82} Copyright [year, publisher]. (b) IMT of VO$_2$ facilitated polarization state modulation of mid-infrared waves. The hybrid metasurface consists of anisotropic plasmonic resonators on VO$_2$ films. Reproduced with permission.\cite{85} Copyright [year, publisher].

It has been known that, taking advantage of the lattice matching condition, a high quality VO$_2$ film exhibiting rapid propagation of the monoclinic-tetragonal phase transformation can be obtained on sapphire substrates through oriented growth. Consequently, VO$_2$ films have been introduced into photonic metasurfaces as a substrate that provide a highly variable dielectric environment.\cite{80,81} Nevertheless, to enable tunable responses in more sophisticated systems based on the IMT of VO$_2$, the fabrication of VO$_2$ on other materials, including those in an amorphous phase,\cite{84} is desirable. For instance, to enable the active response regulation of metasurface absorbers that typically consist of three (metal/dielectric/metal) layers, VO$_2$ films must be grow on metallic or other amorphous thin films. Chandra et al. have demonstrated adaptive infrared camouflage by using VO$_2$ films on a SiO$_2$/Au film, which varies the length of the multilayered cavity and the reflection behavior of the plasmonic system.\cite{86} On the other hand, this VO$_2$ growth flexibility may allow electrical signal based
transition control of VO$_2$ and accordingly facilitate electrically tunable metasurfaces which are regarded as an essential component for practical metadevices.[87] Indeed, electrical current and field-effect induced phase transitions in VO$_2$ have been reported previously, [88,89] though their microscopic origins are still controversial.

By integrating a VO$_2$ thin film into an optical metasurface absorber, Liu et al. have demonstrated a hybrid metasurface platform for electrically triggered multifunctional control in the mid-infrared region.[25] As the schematic in Figure 4a illustrates, the hybrid metasurface consists of two continuous metallic layers sandwiching an active VO$_2$ thin film. Importantly, besides supporting the optical resonant modes, the top nanoengineered Au layer was extended and connected to an external circuit to simultaneously allow Joule heating when electrical current flows across the device. Moreover, compared with the reported systems which rely on VO$_2$ serving as bulk substrates,[80,81] the subwavelength-thick VO$_2$ thin-film (~260 nm that < $\lambda_{res}$/12) in this design acts as part of the resonating system, facilitating photonic enhancement as well as the modulation depth to the greatest extent. Reflectance spectra measured in thermal equilibrium indicated an absolute reflectance tuning up to 80% when the current intensity increased from 0 to 1.20 A (Figure 4b). The corresponding data of a cyclic change in the current provide a clearer presentation of the electrical current dependent reflectance at the two resonances. Accordingly, two types of electro-optic functionality, i.e., reversible reflection switching as well as the memory effect due to hysteresis, were further investigated by applying electrical current pulse trains (Figure 4c). An absolute reflectance switching up to 75% and a reflectance-signal based rewritable memory effect observed at the resonances clearly revealed the phase transition of VO$_2$ enabled dynamic response of the hybrid metasurface. Exploiting the spatial modulation capability enabled by metasurface absorbers, the authors further demonstrated the potential of the proposed hybrid metamaterials for an electrical current controlled infrared display (Figure 4d). As shown in Figure 4e-g, by placing VO$_2$ at the feed gap of each bow-tie antenna, Zhu et al. minimized the thermal mass of the phase change material and demonstrated the electric current based spectral control through the Joule heating effect.[90] Electric current signal controlled continuous resonant wavelength shift, millisecond reflection switching, and dynamic imaging were observed in the near-infrared range. Working as reconfigurable optical filters, metasurfaces integrated with VO$_2$ are also proposed to shape femtosecond optical pulse through Joule heating based phase transition control.[91]
As mentioned above, the IMT of VO$_2$ can be induced optically on a femtosecond time scale (but recovers in a few tens of picoseconds) without a structural phase transition, indicating its potential for enabling hybrid metasurfaces for ultrafast modulation of light. Lei et al. have demonstrated UV-light pulse controlled transmission as well as the corresponding memory effect from a hybrid plasmonic metasurface consisting an array of gold nanodisks on VO$_2$ thin films. Besides the direct transition induced method based on optical absorption of VO$_2$ films, plasmonic resonance enabled field enhancement has been exploited to facilitate low-switching-power ultrafast metadevices. Taking advantage of the localized plasmonic confinement, Muskens et al. have demonstrated that resonant pumping of nanoantenna-VO$_2$ hybrid metasurfaces can facilitate high-repetition, fully reversible switching of the IMT of VO$_2$, which in turn results in picosecond response modulation of the hybrid system in a power efficient manner. By studying the laser-induced heating effect, Li et al. recently have demonstrated the plasmonic-resonance assisted active response from a gold-nanorod assembly coated by VO$_2$ films. In particular, Raman and visible spectroscopy revealed that, compared with bare VO$_2$ films, 28.6% less laser power was required for triggering the IMT of VO$_2$ in Au/VO$_2$ films which can be attributed to the plasmonic enhanced light absorption and photothermal effect. Tian and Li recently reported that the plasmonic enhanced
photothermal effect can also be utilized to realize optically-triggered switchable VO\textsubscript{2}-metasurface absorbers at mid-infrared frequencies. The antenna resonance facilitated modulation at sub-nanosecond time is numerically validated with an optical pumping power about 12.5 times lower than that required by bare VO\textsubscript{2} films.\textsuperscript{[97]}

2.2.2 VO\textsubscript{2} structure based metasurfaces

In addition to incorporation with metallic nanostructures and offering a variable dielectric environment, nanengineered VO\textsubscript{2} structures have been utilized as active building blocks for tunable metamaterials/metasurfaces. Kats \textit{et al.} have demonstrated that a VO\textsubscript{2} thin film on reflective substrates with well-designed thicknesses, which may be viewed as the simplest structural VO\textsubscript{2} metamaterials, can realize temperature tunable mid-infrared perfect absorbers\textsuperscript{[98]} as well as perfect thermal emitters with negative differential thermal emittance.\textsuperscript{[99]} Krishnamoorthy \textit{et al.} have shown that tunable hyperbolic properties can be achieved in VO\textsubscript{2}/TiO\textsubscript{2} heterostructures.\textsuperscript{[100]} Exploiting the temperature dependent phase transition of VO\textsubscript{2}, Sun \textit{et al.} have recently demonstrated a ‘smart’ optical solar reflector consisting of patterned VO\textsubscript{2} on aluminum.\textsuperscript{[101]} At high temperature, this proposed structure exhibits broadband high emissivity in the mid-infrared range due to the plasmonic resonance supported by the metallic-phase VO\textsubscript{2}, while, at low temperature, the VO\textsubscript{2} enters its insulator-phase and the structure presents a much lower emissivity. Consequently, if installed on spacecraft and satellites, the proposed optical solar reflector is expected to maintain system temperature in an optimal range through self-regulated thermal emission according to the device temperature in space. Ito \textit{et al.} reported the emission control of a VO\textsubscript{2} resonator–insulator–tungsten metasurface,\textsuperscript{[102]} while Ligmajer \textit{et al.} recently demonstrated temperature tunable optical responses from an epitaxially-grown VO\textsubscript{2} nanobeam based metasurface.\textsuperscript{[103]} It should be noted that, in addition to the top-down methods, solution-processable colloidal synthesis of VO\textsubscript{2} nanocrystals and assembly techniques that have been reported recently provide an alternative approach to achieving active photonic metasurfaces that exhibit reversible IMT.\textsuperscript{[104]}

It should be noted that as the phase transitions involve lattice rearrangements at an atomic level, VO\textsubscript{2} provides variation of material properties in a broad frequency band. Therefore, VO\textsubscript{2} can facilitate tunable responses from VO\textsubscript{2}-hybrid metasurfaces in the visible regime and longer wavelengths. On the other hand, measured results showed that the plasmon wavelength of metallic VO\textsubscript{2} is around 800 nm,\textsuperscript{[80]} indicating that the material and its structures can support plasmonic responses in the near-IR regime and at longer wavelengths.

3. Indium Tin Oxide (ITO)

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As a widely used transparent conducting oxide, indium tin oxide (ITO) has a carrier density orders of magnitude higher than that of conventional semiconductors such as Si and GaAs. Specifically, the concentration of oxygen vacancies and interstitial metal dopants determines its carrier density which may range from $10^{19}$ cm$^{-3}$ to $10^{23}$ cm$^{-3}$ and can thereby change both the electrical and optical properties of the material. More importantly, the large carrier density of ITO allows pronounced changes in refractive index under external stimuli, such as electric field and optical hot-carrier injection, making ITO a good candidate for reconfigurable photonic systems.

Simple calculations based on the Drude model show that the plasmon frequency ($\omega_p$) of conducting oxides blueshifts as carrier density increases. For instance, as carrier density increases from $10^{21}$ cm$^{-3}$ to $10^{22}$ cm$^{-3}$, $\omega_p$ shifts from $\sim 1.0$ um to $\sim 330$ nm. It was reported that for ITO under strong electric field its plasmon frequency can shift from near-IR to $\sim 400$ nm due to the field induced carrier accumulation.\(^{[105]}\) Nevertheless, it would be challenging to use ITO for plasmonic purposes in the visible due to the corresponding high Ohmic loss. Therefore, ITO is suitable to support plasmon resonances in near-IR regime and at longer wavelengths. It should be noted that, besides ITO, the carrier density, which is dominated by both the materials' intrinsic properties and the doping levels, directly determines the operation wavelength range of many active materials, including graphene and AZO (see discussions in Section 4 and Section 8 for details).

### 3.1 Electrically Tunable

Under an applied electric field, the carrier concentration at a dielectric/conducting oxide interface generally increases due to charge accumulation in a thin layer, which can result in a dramatic modification of the local refractive index. A unity-order refractive index change at visible wavelengths was previously observed at the dielectric/ITO interface under an applied electric field.\(^{[105]}\) Yi et al. have reported that ITO thin film coated gold nanostrip metasurfaces exhibit electrically tunable absorbing behavior.\(^{[106]}\) However, because of the metal-oxide-semiconductor (MOS) configuration used in this work, the charge accumulation that enables refractive index change in ITO only occurs at the area between the metallic nanostructures and consequently only limited tunability was achieved. Electrically-induced carrier density change alters the plasmon frequency of conducting oxides, which enables electrically controllable permittivity sign switching within the so-called epsilon-near-zero (ENZ) region. By embedding ITO into the resonance cavity of a metasurface absorber, Park et al. have demonstrated electrically tunable optical responses from the hybrid system with a modulation depth as large as 15% at wavelengths around the ENZ region of ITO.\(^{[107]}\) The electrically-induced carrier depletion and accumulation facilitate a pronounced tuning effect based on a sign switch of the ITO’s permittivity. By applying a moderate electric voltage (2.5 V)
between top gold nanostrips and the bottom ground plane of a metasurface absorber, Huang et al. have demonstrated a reflection phase shift up to 180°, with a concomitant 30% maximum change in the reflectance spectra. Spatial electrical switching at a modulation frequency as high as 10 MHz was also observed. This demonstrated flexibility in modulating the optical response of antenna-ITO hybrid nanostructures through the electric field effect offers an attractive approach for dynamic control of both the phase and amplitude of optical waves impinging upon such metasurfaces.

Beyond the ENZ region, electric field control can be expected to produce a permittivity change with a larger absolute value in ITO at longer wavelengths. Park et al. have demonstrated electrically active tuning of the reflection phase and polarization of mid-infrared waves reflected from a gold-nanostrip/ITO/Al₂O₃/Au metasurface (Figure 5a,b). By applying a bias gate voltage in the range of -40 V to 40 V, a 180° reflection phase tuning of light at a wavelength around 6 μm was observed. It was verified that this large phase modulation capability can be attributed to the control over the resonant properties of the antennas described by coupled mode theory. Thyagarajan et al. have recently demonstrated that remarkable modulation of a silver/alumina/ITO multilayer metasurface can be achieved with a rather moderate electric field. In contrast to the studies discussed above, the observed plasmonic response tuning arises from optical extinction change due to the electric field triggered transport of silver ions through a 5-nm-thick alumina layer and growth of silver nanoparticles in the ITO counter-electrode, revealing that an alternative modulation mechanism occurs at an applied electric field as low as 1 mV nm⁻¹.

ITO has also been considered as an active medium for electrically tunable dielectric metasurfaces around its ENZ region. In these studies, doped silicon nanostructures were utilized to simultaneously support Mie resonances and the electrical functionality. In particular, the Mie resonances of the silicon resonators were tuned by an external electric field that controls the carrier density of ITO thin layers which is separated by a thin alumina layer from the silicon structures (Figure 5c), or is sandwiched between the Mie resonators and the ground plane (Figure 5d) or electrolyte (Figure 5e,f). (More detailed discussions about tunable dielectric metasurfaces can be found in Section 6).
Figure 5. Electrically active ITO-hybrid metasurfaces. (a) Schematic of nanostrip based absorber design for reflection phase control from 0° to 180°. (b) Measured spectral dependence of reflection phase of light for three different bias conditions (left) and the phase of the reflected light at a wavenumber of 1680 cm⁻¹ as a function of the biasing voltage. Reproduced with permission. Copyright [year, publisher]. (c-d) Schematic of two designs for electric field-controlled ITO-dielectric metasurfaces. Reproduced with permission. Copyright [year, publisher]. (e) Schematic of electrolyte based ITO-dielectric metasurfaces. (f) Measured transmittance spectrum and IR camera images of the fabricated device at three distinct applied bias voltages. Reproduced with permission. Copyright [year, publisher]. Si nanostructures were used to simultaneously support optical resonances and electrical functionality, which allows electrically tunable responses from the metasurfaces based on the ITO’s tuned carrier density.

3.2 Optically Tunable

As mentioned above, the optical properties including the plasmon frequency of ITO are determined by the carrier density of the addition of n-type dopants. The incorporation of plasmonic nanoantennas has previously demonstrated picosecond optical excitation of ITO with local modulations of the free-carrier density which suggests a distinct approach for developing ultrafast metadevices with all-optical switching capability. The nonlinear response of a typical
nanoantenna-ITO hybrid system may involve multiple processes, in which transportation of plasmon-mediated hot-electrons act as a local source of ITO’s nonlinearity that in turn modifies the plasmon response of the nanoantennas. In contrast to electrically tunable metadevices whose maximum modulation speed is primarily limited by their circuit response, optical carrier injection in ITO allows ultrafast switching of hybrid metasurfaces.

Based upon a mechanism analysis of the generation and thermalization of plasmonically induced hot-electrons in nanostructure systems, Taghinejad et al. have recently demonstrated a fast relaxation pathway that originates from the extraction of hot-electrons from plasmonic nanoantennas during the electron-electron scattering process. Accordingly, by incorporating ITO as the electron acceptor material in a plasmonic lattice that exhibits localized plasmon (LP)
resonance, the authors have demonstrated a femtosecond (~190 fs) optical modulation in ITO-gold metasurfaces, overcoming the constraint of the picosecond-scale response time in previous studies that were limited by the slow electron-photon interaction. In stark contrast to the Fabry–Pérot (FP) resonance exhibiting highly confined modes, excitation of the LP resonance that is intrinsically subradiant results in a large population of hot-electrons in the conduction band of gold, which provides the basis for optical Kerr nonlinearity in ITO. Importantly, the observed femtosecond response time originates from the on-resonance excitation of the LP resonance and the corresponding electron-dominated relaxation channel that is facilitated by the exchange of plasmonically induced hot electrons at the gold antenna/ITO interface. Taghinejad et al. recently have further demonstrated that, besides the intensity modulation, the ITO-hybrid metasurfaces can also be used to achieve polarization state control of light in an ultrafast femtosecond regime.\[118\]

In fact, recent studies on the optical nonlinearity of ITO reveal that more dramatic modulation of ITO integrated metasurfaces can be expected in the region around the ENZ frequency of ITO. Alam et al. have shown that, in the nonlinear regime, both the real and imaginary parts of the refractive index of an ITO film are highly wavelength dependent.\[119\] Relative to a wavelength (e.g. 970 nm) away from the ENZ frequency, a more than 40 and 50 times enhancement in the effective nonlinear refractive index coefficient ($n_2(\text{eff}) = \Delta n/\lambda$) and effective nonlinear attenuation constant ($\beta(\text{eff}) = \Delta \alpha/\lambda$) was observed at the ENZ wavelength (1240 nm), respectively. Moreover, as illustrated in Figure 6c, for TM-polarized light at oblique incidence a change in the real part of the refractive index as large as ~0.72 was identified. A temporal dynamics study showed that this index change is reversible with a rise time and recovery time of ~200 fs and ~360 fs, respectively. Furthermore, by incorporating nanoantennas on ITO thin films, the same group recently has demonstrated an ultrafast intensity-dependent effective nonlinear refractive index up to $-3.73 \pm 0.56$ cm$^2$ GW$^{-1}$ within a 400 nm of spectral span around the ENZ wavelength of ITO, as well as a broadband change in the system’s refractive index of ± 2.5 (Figure 6d).\[120\] In addition to a resonance enabled optical field enhancement that reduces the light intensity required, the introduction of nanoantennas also determines the linear dispersion of the system and provides an efficient mechanism for the coupling between normal incident light and the ENZ films. These studies suggest that the integration of ITO into a CMOS-compatible degenerate semiconductor that exhibits large ultrafast nonlinearity and plasmonic structures may provide the basis for achieving optically switchable photonic systems in the near-infrared region.

4. Graphene
4.1 Graphene-hybrid Metasurfaces

As a zero bandgap two-dimensional (2D) material, graphene provides a rather unique opportunity for achieving ultra-compact and highly tunable metasurfaces. For actively controllable plasmonics, the most attractive property of graphene is the electrically tunable dielectric functions originating from its highly tunable carrier concentration under an applied electric field. Given the fact that the plasmonic resonance of nanostructures is extremely sensitive to the dielectric environment in its proximity, changes in the dielectric property of graphene that even though it is a single atom thick can have a significant influence on the optical response of hybrid metasurfaces. There have been a number of studies on graphene enabled active plasmonic metasurfaces and two recent review papers have provided a comprehensive description of the development of this research.\cite{121,122}

The remarkable electric field effect on graphene's electronic as well as optical properties can be understood from band structure and transition analyses.\cite{122} In brief, the hexagonal lattice structure of graphene leads the conduction and valance bands to touch, which allows the excitation of both intraband and interband transitions under photon illumination. The Fermi energy ($E_F$) of graphene can be described by $E_F = \hbar v_F (\pi n_{g,2D})^{1/2}$, where $\hbar$ and $v_F$ are the reduced Planck constant and the Fermi velocity of electrons, respectively, while $n_{g,2D}$, the carrier concentration in the 2D graphene sheet, can be electrically tuned via an applied gate voltage. On the other hand, the complex permittivity ($\varepsilon_g(\omega)$) of graphene has a simple relation to optical conductivity ($\sigma_g(\omega)$), i.e.,

$$\varepsilon_g(\omega) = i\sigma_g(\omega)/[\omega - i\tau_0 t_g],$$

where $t_g$ is the thickness of the graphene sheet. To address both photon induced transitions, $\sigma_g(\omega)$ of graphene can be derived within the framework of the random-phase approximation (RPA) in the local limit\cite{124,125} as

$$\sigma_g(\omega) = \frac{2e^2 \omega_F}{\pi \hbar} \frac{i}{\omega + i\tau} \log \left[ 2 \cosh \left( \frac{\omega F}{2\omega_T} \right) \right] + \frac{e^2}{4\hbar} \left[ H \left( \frac{\omega}{2} \right) + \frac{2\omega}{\pi \gamma_0} H \left( \frac{\omega}{2} \right) \frac{H'(\frac{\omega}{2}) - H'(\frac{\omega}{2})}{\omega^2 - \omega^2} d\omega' \right],$$

where $H(\omega) = \sinh \left( \frac{\omega F}{2\omega_T} \right) / [\cosh \left( \frac{\omega F}{2\omega_T} \right) + \cosh \left( \frac{\omega T}{2\omega_T} \right)]$.

Beyond spectrum modulation, more recent studies on graphene-hybrid metasurfaces have been focused on the advancement of more sophisticated functionalities.\cite{132-136} The gate-tunable resonances observed imply that graphene-loaded metasurfaces may be used for comprehensive manipulation of both amplitude and phase properties of light waves. Sherrott et al. have recently
investigated the electrically controlled mid-infrared reflection phase at the interface between air and a graphene-gold metasurface absorber.[132] Operating at wavelengths around the highly absorptive region dominated by the gold nanoantennas, the hybrid metasurface showed continuous reflection phase tuning up to 230° (Figure 7a), indicating a larger phase modulation depth compared with that observed in previous graphene- and ITO-hybrid metasurfaces. Based on electrostatically gate-tunable phase modulation,[137] graphene-hybrid anisotropic metasurfaces have been used to achieve control over polarization state including the ellipticity and tilt angle of mid-infrared light.[133]

Modulation speed and depth are in general the two main factors for evaluating the performance of an electro-optic modulator. Although theory and experiments have revealed that graphene supports ultrafast opto-electronic responses, examples of graphene-loaded metasurfaces that allow high speed dynamic control of optical signals remain rare. The response time is primarily limited by the circuit parameters at the device level. By reducing the device capacitance, Zeng et al. have recently reported field-effect transistor (FET) configuration based graphene-hybrid metasurfaces for high speed and broadband mid-infrared modulation.[135] In particular, a dielectric spacer comprised of a combination of two layers, an α-Si layer that serves as part of the gate electrode for low frequency gate voltage and an ultrathin alumina layer functioning as an insulator at both gating and optical frequencies, was sandwiched between the graphene layer and the ground plane. The advantage of this strategy is three-fold: (i) the combined spacer supports optical absorption modes at mid-IR operating wavelengths, which ensures pronounced modulation depth; (ii) at the gating frequencies, the gate voltage is directly applied to the thin alumina layer, which largely reduces the (capacitance) response time of the metadevice; and (iii) simultaneously, it decreases the voltage amplitude required by the electro-optic tuning of graphene. With these design criteria in mind, in the absence of the loaded external resistor the authors observed a modulation speed exceeding 1.0 GHz over a broad bandwidth at a moderate gate voltage bias of ~7 V. Furthermore, taking advantage of the spatially selective absorptivity supported by the absorber mode, the authors also demonstrated a prototype of a graphene-hybrid metasurface based spatial light modulator for high frame rate single-pixel imaging.
Figure 7. Graphene-loaded electrically tunable metasurfaces. (a) Schematic of a graphene-based gate-tunable metadevice for control of reflected phase (top left), SEM image of a fabricated gold nanorod array on graphene (bottom left), and the measured phase modulation at different gate voltages corresponding to indicated Fermi energies (right). Reproduced with permission. [132] Copyright [year, publisher]. (b) Graphene-integrated anisotropic metasurfaces for polarization control. Schematic of the metadevice (top), measured anisotropic reflectance spectra (bottom left) and the polarization ellipses at λ = 7.76 μm (bottom right) at gate voltage of -200, 0 and 250 V. Reproduced with permission. [133] Copyright [year, publisher]. (c)–(e) Graphene-hybrid metasurfaces for high-speed light modulation and single-pixel imaging. Schematic of the corresponding metadevice ((c), left) and reflection spectra at different gate voltages ((c), right). Electrical modulation speed under different device circuit conditions (d). Inset: schematic of the modulation speed measurement system. An optical microscopic image and a photograph of the fabricated metadevice ((e), top left), spatial reflection patterns at λ = 8.3 μm obtained by controlling gate voltage applied on individual pixels ((e), bottom left), schematic of the single-pixel imaging setup ((e), top right) and the reconstructed images of a cross-shaped object at a series of wavelengths ((e), bottom right). Reproduced with permission. [135] Copyright [year, publisher].

4.2 Graphene Structure Base Metasurfaces

Due to its excellent compatibility with CMOS processing and broadband response, nanopatterned graphene structures can directly enable strong light-graphene interaction arising from the excitation of localized surface plasmons in graphene. Compared with metallic nanostructures, the use of graphene-based metasurfaces can significantly decrease fabrication complexity. Accordingly, metasurfaces composed of nanopatterned graphene building blocks that
facilitate graphene plasmonics have attracted considerable attention with regard to their potential for electro-optic metadevices.\textsuperscript{[138–140]} Three review papers have summarized the successes of the early developments in this field.\textsuperscript{[141–143]} Recently, theoretical studies have predicted that graphene nanogratings can be used to achieve well-controlled phase of light waves for a broadband lensing effect\textsuperscript{[144]} and gate-voltage tunable perfect absorption.\textsuperscript{[145]} A theoretical study has revealed that the interaction between graphene supported plasmons and DC current flow in a system provides a novel mechanism for graphene based light manipulation.\textsuperscript{[146]} By engineering the intrinsic carrier transport asymmetry and the lifetime of a graphene layer as well as the depletion region of silicon, Chang \textit{et al.} recently have demonstrated a graphene-silicon Schottky junction based photodector with a photoresponsivity as high as 70 A·W\textsuperscript{−1}.\textsuperscript{[147]} As discussed in Section 2, the carrier density determines the plasmon frequency $\omega_p$ of conducting materials. Consequently, graphene can well support plasmonic responses in the mid-IR and at longer wavelengths due to its intrinsic carrier densities in the range $10^{11} - 10^{13}$ cm\textsuperscript{−2}.

5. Liquid Crystals (LCs)

A significant research area for tunable optical metamaterials/metasurfaces is that of liquid crystal (LC) augmented devices. Due to their molecular structure, LCs may be leveraged to introduce a significant amount of optical anisotropy into the unit cells which incorporate them, which may be used to produce many different effects. The intrinsic rod-shape of LC molecules enables their interaction with electromagnetic waves to be significantly affected by the polarization of the wave with respect to the long dimension of the molecule, called the director axis. In particular, LC molecules can form a variety of arrangements, referred to as phases, which affect the director axis in different ways and produces optical anisotropy in the material. There are several types of LC phases, including nematic, smectic, blue-phase, isotropic, etc., each of which instill varying degrees and types of order on the molecules. The smectic phase, for instance, maintains positional and orientation order, whereas nematic only preserves orientation order, and isotropic is unordered. An immediate application of LC phase transitions has been that of tunable effective material properties, like a tunable negative index metamaterial in the near-IR,\textsuperscript{[148–150]} or all-dielectric and metallo-dielectric negative through sub-unity index change in the mid-IR,\textsuperscript{[151]} among others. In more recent years, researchers have successfully applied LCs to a wide variety of optical metasurfaces to produce a host of other interesting effects.

The phase of a LC depends on several factors, including the chemical composition of its constituent molecules, its temperature, and critically, the local electrical/magnetic conditions. While some designs explicitly rely on changes in the temperature of the unit cell for tuning,\textsuperscript{[152,153]} most
induce changes on the liquid crystal electrically by applying voltage or by irradiation, often ultraviolet (UV). LC molecules will in general align with an impressed electric field, which allows for the material phase to be modified using an appropriately oriented external voltage or by illumination at a specific frequency and polarization. In addition to affecting the anisotropy of the material, phase changes in an LC can also alter the plasmonic behavior of nearby metals. This makes LCs an attractive tuning medium to apply to optical metasurfaces. Using these mechanisms, many different tuning effects can be achieved for metasurfaces which integrate LCs.

Modification of an incident wave’s phase is an immediate application of adjustable anisotropy that can allow applications like electrically controlled zoom using an LC layer or temperature tuned laser steering when the LC on dielectric metasurface transitions from nematic to isotropic. Transmissive phase delay has been observed in a LC tuned metasurface which modifies the Tamm-plasmon resonance between a photonic crystal and metallic film, an optically addressed non-pixelated spatial light modulator that used a reversible photoalignment of LC with a light sensitive azobenzene layer for potential use in phase-contrast microscopy, and a LC enhanced voltage tunable dielectric metasurface lattice structure which exhibits polarization dependent electromagnetically induced transparency (EIT) among others. Reflective phase delay has similarly been identified in a temperature or voltage controlled metasurface-like self-organizing chiral LC in the visible spectrum. Using a tunable chiral LC, Buchnev et al. were able to tune transmissive polarization rotation by electrically twisting the LC above a plasmonic zig-zag metasurface structure.

Another commonly studied LC tunable metasurface effect is that of continuous resonance modulation. In Ref[145], an electrically tuned Mie-resonant dielectric metasurface of silicon nanodisks embedded in twisted nematic LCs exhibited a spectral shift between two transmission states, amounting to a change of 75% in the transmission band. In an alternate approach, a zig-zag metasurface was suspended in LC and charged to untwist the LC and generate a 110nm transmission red-shift. Explicit plasmonic interaction between the LC and metasurface has also been used to create a voltage tunable plasmon induced transparency effect, voltage tunable dynamic plasmonic color filter using an aluminum grating, and a polarization-independent tunable reflection color modulating nanostructure which can be seen in Figure 8a. Lee et al. showed that a color-tunable mirror can be voltage controlled by broadening the CP bandwidth of a polymer-stabilized cholesteric LC layer. Some designs forgo continuous tunability and instead select between a pair of resonances. For instance, as shown in Figure 8b, a twisted nematic LC was used to create a 120nm separated two-state filter by rotating the incident field and filtering it against an asymmetric array of nanoholes in a metal film. Similarly, a thermally tunable all-
dielectric metasurface used dielectric pucks embedded in a LC that tunes a pair of filtering bands, and a nanoscale dual split-ring resonator was used to generate two resonances in the near IR that were selected between using a twisted nematic LC that was irradiated with UV light. (More detailed discussions about tunable dielectric metasurfaces can be found in Section 6).

LCs may also be used in the tuning of grating metasurfaces. Chen et al. used electrically controlled LCs to modify the diffraction efficiency of a binary-grating and Yan et al. used a polymer stabilized blue-phase LC to tune a phase grating. A dye-doped LC cell was also used for creating an optically erasable fishnet structure by illuminating it with two orthogonal interference fields for potential use as a controllable photonic crystal. Metasurfaces have also been used in the past to create non-reciprocal transmission and reflection boundaries, and LCs allow for such surfaces to be tuned actively. In one case, a hetero-periodic band gap (PBG) structure using nematic LC sandwiched between two cholesteric LC layers with different helical pitches produced switchable non-reciprocal transmission of CP light in the bandgap region. A recent work also showed that a twisted nematic LC cell in a meta-pixel based metasurface could control asymmetric reflectance and transmittance, as shown in Figure 8c. LCs have also been used for voltage controllable absorbers, such as Xiao et al.’s investigation of a voltage tunable liquid-crystal-loaded chiroptical multiband absorber.

While the work described above, which represents a cross-section of the latest work on tunable optical metasurfaces, demonstrates a wide variety of effects and applications of LCs, the possibilities of LCs in optical metasurfaces is a deep subject with much more work to come. Other recent publications have similarly gone in-depth about research being conducted in the specific area of tunable LC metamaterials/metasurfaces, and so may be another good source for readers interested in learning more about this field. Furthermore, it should be noted that, arising from the molecules’ rotation under external stimulus, the tuning effects of liquid crystals are extremely broadband. For instance, besides the reconfigurability in the optical regime summarized here, liquid crystals have also been used to facilitate tunable metamaterials at THz and microwave frequencies. However, it should also be noted that liquid crystals are not suitable for applications requiring drastic and/or fast tuning due to their limited optical anisotropy and relatively slow response.
Figure 8. Tunable metasurfaces based on LC phase changes. a) LC modulated reflected structural color. Voltage controlled LC tunes reflection wavelength in image (bottom). Reproduced with permission. Copyright [year, publisher]. b) Tuning reciprocity of transmission/reflection using zigzag and twisted nematic LC. Transmission spectra tunes depending on the orientation of the surface. Reproduced with permission. Copyright [year, publisher]. c) Modulating transmission frequency with twisted nematic and hole metasurface. Twisted nematic phase rotates incident field and hole metasurface filters to produce a color shift. Transmission spectra for different voltage biases shown at the bottom. Reproduced with permission. Copyright [year, publisher].

6. Tuning Dielectric Metasurfaces with Variable Constituent Properties

Dielectric resonators with subwavelength dimensions as an alternative to metallic structures (such as SRRs) were first explored at microwave frequencies to investigate their Mie resonance based low loss magnetic and electric responses. Isotropic negative permeability and negative refractive index were experimentally observed in metamaterials composed of high index ceramic resonators. In optics, due to the intrinsic loss of plasmonic structures that support subwavelength modes as well as the dispersion of metals that prevent the geometric scalability of metallic resonators, dielectric meta-atoms are cherished because of their important roles in manipulating light with extremely low loss. Combined with the capability of supporting sophisticated optical modes with simple shapes (e.g. magnetic resonance of nanospheres or nanocylinders), dielectric
resonators offer opportunities to achieve nanophotonic devices based on simple fabrication processes. Two important review papers on Mie resonance enabled meta-optics and nanophotonics were recently contributed by Kivshar’s group.\[181,182]\ Here we will focus on the recently reported dielectric metasurfaces with dynamic tuning capability offered by different mechanisms in both the linear and nonlinear regimes.

Mie resonances originating from the displacement current oscillation induced by incident electromagnetic waves in the dielectric structures are capable of dramatically boosting the structure’s light-matter interaction due to field enhancement effect in the resonators. It is known that in the Mie resonance region the magnetic resonance (the lowest frequency mode) of a dielectric sphere (of radius $R$ and index $n$) occurs at a wavelength $\lambda$ satisfying $2R = \lambda/n$. This indicates that a larger ratio between the operating wavelength and resonator dimensions can be achieved when a higher refractive index is used. However, in contrast to lower (such as microwave and THz) frequencies, in the optical regime indexes of materials, like semiconductors (e.g. silicon (Si), germanium (Ge) and gallium arsenide (GaAs)), are generally rather moderate, resulting in two important facts. First, according to the scattering theory of particles that are small relative to the incident light wavelength, a series of resonances corresponding to a variety of multipole modes may be observed in the scattered field of an isolated dielectric sphere under illumination by linearly polarized light. The coupling between the multipole modes, which is referred to as the coherent effect, is primarily determined by geometries and dielectric properties of the particles. Resonators of lower permittivity show an increase in the coherent effect, represented by the scattering spectral features which correspond to the multipoles being close to each other.\[183]\ Second, the corresponding response of the metasurfaces cannot be appropriately described by the effective material parameters but can be analyzed under the concept of “meta-optics”\[182]\ Nevertheless, the semiconductor nature of these materials, including the low loss at wavelengths of energy below their bandgap and the refractive index tuning capability, make the corresponding dielectric metasurfaces an ideal platform for active photonics in both the linear and nonlinear regimes.

The response of Si (and Ge) resonators can be largely modulated through doping based carrier concentration control,\[183]\ although this ‘static’ tuning approach cannot be utilized in applications demanding real-time response modulation. Harnessing the temperature dependent energy gap of Si, Rahmani et al. recently demonstrated the reversible thermal response tuning of Si metasurfaces that were heated up to 300 °C.\[184]\ The observed temperature-dependent refractive index change of Si is pronounced, although the thermal modulation is generally a slow process. This thermo-optic effect of Si nanostructures has been utilized to realize spatial light modulation around the communication...
wavelengths at frequencies up to 10 kilohertz.\textsuperscript{[185]} On the other hand, optical carrier injection provides a more attractive approach for achieving response tuning of dielectric metasurfaces in an efficient manner\textsuperscript{[186–189]} by using femtosecond (fs) laser pulses that lead to ultrafast free carrier density change in semiconductors as well as other possible physical processes, such as two-photon absorption (TPA) and lattice heating.\textsuperscript{[189]} Exploiting the ultrafast TPA process, Shcherbakov et al. have identified a 65 fs-long transmission switching effect in a hydrogenated amorphous silicon ($a$-Si:H) metasurface\textsuperscript{[187]} around the magnetic Mie resonance of the nanodisk resonators. In order to produce more efficient all-optical modulation, Shcherbakov et al. recently fabricated a nanopillar array of GaAs/AlGaAs heterostructures and demonstrated a picosecond-scale absolute reflectance tuning of up to 0.35 around the magnetic Mie resonance supported by the GaAs nanodisks.\textsuperscript{[190]} This work reveals that the two main mechanisms (i.e., the band filling effect and the Drude term) responsible for the refractive index change of GaAs, along with the resonance enabled field enhancement in the resonators significantly reduce the pump fluences required for the observed large modulation of the metasurfaces.

Mie resonances of semiconductor resonators have been exploited to enable enhanced nonlinear harmonic generation signals.\textsuperscript{[191–200]} Compared with the plasmonic resonance associated with metallic nanostructures, the locally enhanced field of Mie resonances occurs primarily within the dielectric resonators, which results in large modal volume that can remarkably increase the nonlinear generation efficiency. Yang et al. have reported strongly enhanced third harmonic generation from a Fano-resonant Si metasurface, in which the more than $10^5$ times larger nonlinearity relative to an unstructured Si film was essentially attributed to two factors, the high $Q$-factor Fano resonance enabled local field enhancement and the suppressed two-photon absorption effect due to the subwavelength nature of the disk-like resonators.\textsuperscript{[191]} In addition, a comprehensive engineering of magnetic and electric dipoles and quadrupoles provides a novel approach to control the radiative and nonradiative lifetime of optically injected carriers in Si nanoparticles, enabling high-quantum-efficiency white-light emission from the metasurfaces and individual building blocks.\textsuperscript{[198]}

Spatial dispersion design capability of metasurfaces has been introduced as a method of wavefront shaping in both linear and nonlinear regions.\textsuperscript{[9,10,53,201]} Based upon the wavefront control over third harmonic generation (THG) from subwavelength silicon resonators, Wang et al. recently have demonstrated dielectric metasurface enabled nonlinear beam-deflectors and vortex beam generators.\textsuperscript{[192]} In particular, a Mie theory based multipolar method was implemented as an efficient means for analysis of nonlinear scattering properties of the dielectric resonators, including both phase and amplitude of the THG waves. Although, compared with silicon, GaAs possesses much larger second order nonlinear susceptibilities ($\chi^{(2)}_{ij,k}$), two factors impede access to the strong optical
nonlinearity of bulk GaAs materials. First, the $\chi^{(2)}_{ijk}$ tensor that only contains off-diagonal components, and second, the symmetry of GaAs’s zincblende lattice structure. Nevertheless, recent studies have shown that the local field manipulation ability offered by Mie resonances can dramatically boost the nonlinear generation from nanoengineered GaAs metasurfaces, in which the nonlinear signals were resonantly enhanced and closely dependent on the excitation conditions such as the polarization of pumping light\cite{195,197} or the relative time relation between excitation pulses.\cite{199} Utilizing a leaky resonance excited in a dielectric resonator lattice, Ha et al. recently have reported a directional lasing phenomena in metasurfaces composed of GaAs nanopillars.\cite{200} The identified low-gain lasing effect arises from the so-called bound state in the continuum (BICs) that is based on the collectively excited vertical electric dipole resonance in the nanopillar arrays. Importantly, this study also showed that by combining the tuning mechanisms originating from lattice structure and temperature variation, the proposed metasurfaces can realize directional lasing at selected angles and wavelengths.

**Figure 9.** Dielectric metasurfaces enable enhanced optical nonlinearity. (a) Silicon metasurfaces as nonlinear beam deflectors and nonlinear vortex beam generators. Schematic of silicon nanopillar based metasurfaces for wavefront control of third harmonic waves (top), directionality diagram and the corresponding cross-section of the forward TH wave generated by a metasurface deflector (bottom left), and the donut-shape cross-section of the TH beam generated by a metasurface vortex beam generator (bottom right). Reproduced with permission.\cite{194} Copyright [year, publisher]. (b) GaAs metasurfaces based optical frequency mixer. Schematic of the GaAs resonator array based metamixer (left), nonlinear spectrum when the GaAs metasurface is simultaneously pumped by two optical beams at $\lambda_2 \sim 1.24 \ \mu m$ and $\lambda_1 \sim 1.57 \ \mu m$ (top right), and intensities of the sum-frequency generation ($\omega_1 + \omega_2$), four-wave mixing ($2\omega_2 - \omega_1$), and six-wave mixing ($4\omega_1 - \omega_2$) as a function of the power of the $\omega_2$ pump (bottom right). Reproduced with permission.\cite{199} Copyright [year, publisher]. (c)-(d) GaAs nanopillar based metasurfaces for directional lasing. Schematics of the system (left in
(c)) and the vertical and horizontal resonance modes supported by a dielectric nanopillar (top right in (c)), and SEM images of the fabricated sample (bottom right in (c)). Evolution of normalized emission spectra as a function of pumping fluences (left in (d)) and the temperature based wavelength tunable lasing effect in the dielectric metasurfaces. Reproduced with permission. Copyright [year, publisher].

7. Mechanically Tunable Metasurfaces

Since metasurfaces derive their optical properties from engineered structures and the geometric arrangement of their resonant building blocks, for a given fixed material composition their responses are closely dependent on their structural properties. In other words, altering the meta-atoms’ shapes and/or spatially varying their arrangement is a powerful means of regulating the response of metasurfaces. Here, we understand the structural variation based tuning of metasurfaces as mechanical in nature. Accordingly, in the first part of this section, we review several reconfigurable metasurfaces achieved by top-down fabrication methods, where the changes in the metasurfaces’ structures mainly arise due to a variety of actuations from two types of forces, i.e., elastic force and electromagnetic force. Ref[191] provides a good review of reconfigurable nanomechanical photonic metamaterials and therefore, in this section we focus on more recent developments in this direction. In the second part of this section, we review recent studies on tunable photonics based on directed assemblies of nanoparticles, which has led to an emerging approach to exploring active metasurfaces facilitated by bottom-up fabrication approaches. It should be noted that, in sharp contrast to tuning effects based on the optical property change of active media, structural variation enabled tunability ought to be applicable to a wide variety of metasurfaces operating at different wavelength ranges.

7.1 Elastic Force Based Metasurfaces

Elastic deformation describes the uniform and recoverable shape change of a material at low stress. Consequently, pronounced response modulations have been observed in metasurfaces via the elastic deformation of the compliant elastomeric substrates. Polydimethylsiloxane (PDMS) a silicon-based organic polymer has been widely used as an elastomeric substrate primarily due to its low optical loss and excellent elasticity which allows for both stretching and compression based reversible deformation. In general, the resonant meta-atom (e.g., SRR or high-index dielectric resonator) arrays fabricated via top-down nanofabrication methods on a commonly-used substrate (such as a silicon wafer) can be transferred to PDMS with the stamping process. One can eventually obtain free-standing meta-atoms-in-PDMS samples by stripping (or peeling off) the PDMS membrane or etching the original substrate used for top-down fabrication. It should be noted that,
thanks to the recent progress in stretchable electronics fabrication, high resolution features of the embedded structures achieved using top-down nanofabrication techniques can be well preserved in the final flexible metasurfaces after the transferring process.

In addition to the studies focusing on the capability of tuning scattering properties (e.g. transmission and reflection) of meta-atoms embedded in elastomeric substrate, mechanical tunability of other fundamental properties of metasurfaces, such chirality, artificial color (Figure 10c), as well as the device level functionalities such as lensing effects have been reported recently. Kamali et al. have demonstrated the strain dependent focal length of a meta-lens composed of amorphous silicon (α-Si) resonators encapsulated in a thin PDMS membrane. Due to the high index contrast between the α-Si resonators and their surrounding medium, there is only weak coupling between the α-Si resonators. This simplifies the metasurface design and more importantly leads the focal distance tuning to follow a simple relation with the strain value ε, i.e., $f_ε = (1 + ε)^2 f_0$, where $f_0$ is the focal length when no strain is applied. The measured optical intensity profiles (Figure 10a) clearly show the close dependence of the focusing properties of the meta-lens on the applied radial strain. By patterning Au nanorods with ~100 nm feature size on a PDMS substrate, Ee and Agarwal have demonstrated a meta-lens operating at visible frequencies with a mechanically tunable focal length. The focal length tuning of the proposed meta-lens satisfies the simple relation discussed above (Figure 10b), indicating a common mechanism shared by the two observed phenomena. Kim et al. have reported reconfigurable chiroptical response (Figure 10d) from nanocomposites that were obtained by conformally coating twisted PDMS substrates with gold nanoparticle multilayers. This study revealed the chirality transfer from microscale to nanoscale due to the elastic properties of the substrate, which provides an alternative approach to the realization of strong chiral response in the optical region. Besides PDMS enabled systems, elastic force based tunability is also observed in other photonic nanostructures. Using soft polymer materials, microelectromechanical systems (MEMS) based mechanical tuning has also been reported, which offers photonic response modulation at the device level. Roy et al. have demonstrated MEMS enabled active beam steering in a metasurface-based mid-IR flat lens. Furthermore, thermally activated optical memory from a photonic metasurface consisting of nanowires comprised by a shape-memory alloy (nickel-titanium) have also been recently demonstrated.
Figure 10. Elastic deformation based reconfigurable metasurfaces. (a) Measured optical intensity profiles when a series of radial strain is applied to the metasurface microlens composed of amorphous silicon resonators encapsulated in a thin PDMS membrane. Inset: An overview of the fabrication steps and an enlarged SEM image of the device. Reproduced with permission.[213] Copyright [year, publisher]. (b) SEM and measured optical intensity profiles of the stretchable metasurface lens. Inset: Schematic of the metasurface on stretched PDMS substrate. Reproduced with permission.[214] (c) Elastic force enabled dynamic image switching of metasurfaces. SEM and white-light CCD images of as-fabricated patterns before transferring process (left three columns) and dark-field images when the patterns are under different stretching conditions (right three columns). Reproduced with permission.[211] Copyright [year, publisher]. (d) Strain-modulated chiroptical response in AuNP multilayers. The procedure to obtain the samples exhibiting chiral response of the opposite handedness (top row), measured CD spectra of samples under different strain (bottom left) and the corresponding peak CD values for five cycles of reversible stretching (bottom right). Reproduced with permission.[210] Copyright [year, publisher].

7.2 Electromagnetic Force Based Metasurfaces

Electromagnetic force for the realization of mechanically active metasurfaces can be categorized into four types, i.e., Coulomb force, Ampère force, Lorentz force and optical force, which are associated with electric potential, current, external magnetic field, and optical excitations in the systems respectively.[205] Although theoretically the four possible types of mechanism can all provide bases for tuning nanophotonic systems, they are, implementation-wise, not equal. The Ampère force requires electric current that may cause undesired issues such as the thermo-optical effect, the control signal of the external magnetic field is inconvenient to generate, and the optical force is in general weak. Consequently, to date most reported studies on electromagnetic forces based tunable
metasurfaces utilized Coulomb force. As shown in Figure 11a, Cencillo-Abad et al. applied a voltage between a nanopatterned metallic layer and the ground plane and demonstrated a dynamic Salisbury screen, in which the electrostatic force was balanced by the restoring force of the elastic structure. Due to the largely tunable cavity length enabled by the electro-mechanical actuation, multiple coherent cases were experimentally identified with an in-depth absorption modulation. As axial distance is critical for imaging performance of multi-lens systems, electromagnetic force has also been used to demonstrate tunable metasurface doublets that exhibit tunable focal lengths. As shown in Figure 11(b), a varying of the axial distance was achieved by applying a direct-current (DC) voltage on the metallic arc structures that were concentric to the dielectric metasurface based micro-lenses. Alternatively, by controlling the radial position of α-Si nanoposts embedded in a membrane of carefully selected elastomer, She et al. have recently demonstrated large-area metalenses with electrically tunable focal length, and importantly, the authors have also shown the capability of correcting the on-the-fly astigmatism and image shift. As shown in Figure 11(c), flexibility in collectively rearranging the α-Si resonators in the metasurface lens was offered by four separately located electrodes (V₁ – V₄) around the microlens that is mounted on the central electrode (V₅). It is evident that the design of electromagnetic forces offers more degrees of freedom for achieving active and reconfigurable optical responses of metasurface based devices. (More detailed discussions about tunable dielectric metasurfaces can be found in Section 6).

![Figure 11](image)

**Figure 11.** Electromagnetic force based tunable metasurfaces. (a) Schematic cross-section of the dynamic Salisbury screen (top) and its unit cell (bottom right) and the SEM image of the fabricated metasurface. Reproduced with permission. Copyright [year, publisher]. (b) Schematic of the imaging setup using a regular glass lens and the tunable doublet (top) and the corresponding imaging results with a series of applied voltage (bottom). Reproduced with permission. Copyright [year, publisher]. (c) Schematic illustration of the DEA metasurface (top) and the measured intensity profile indicating the tunable focal lengths of the metasurface microlens. Reproduced with permission. Copyright [year, publisher].

7.3 Directed Assembly Based Metasurfaces
Nanoparticles (NPs), especially plasmonic nanostructures such as nanospheres (NSs), nanorods (NRs) and nanowires (NWs) of noble metals, are of great interest because of their superb optical properties and potential applications in photonic devices. Control over the organization of NPs and NP mixtures has been used to generate photonic systems exhibiting novel optical properties that are imparted by the collective response of the array. Recent developments in NP assembly methods provide a powerful means of achieving well-organized, mixed-population NP systems which bring about photonic devices whose functionality is dependent upon multiple and specific NPs. Importantly, considering that the collective response relies on characteristics of the assemblies such as density, arrangement, and orientation, post-assembly component reorganization could enable tunability of this type of system. Therefore, compared with their top-down fabrication counterparts which have been widely used in the fabrication of photonic metasurfaces, bottom-up NP assembly provides a promising route for cost-effective, large-area photonic architectures with reconfigurable functionalities. As the relevant topic has been discussed in a few recent review papers,[222–224] here in this section we will focus on the most recent studies in the field of assembly based reconfigurable photonic nanocomposites.

The key to active assemblies is to introduce stimuli that alter the NPs’ organization. Electric field,[225] laser pulses[226] and chemical treatment[227–229] have been recently used to achieve dynamically tunable optical properties of NP assemblies. Exploiting dielectrophoresis (DEP) enabled requisite control over particle orientation and placement, Boehm, et al. have demonstrated an electric-field-switchable broadband polarizer based on gold NW assemblies.[225] Experiments have shown that gold NWs may align along the electric field gradients due to their negative DEP and create organized structures, while the corresponding lattice periodicity and formation vary with the strength and frequency of the AC field in real-time.[230] The geometrical anisotropy of gold NWs translates into an anisotropic optical response of the gold NWs, which can be clearly seen from its polarization sensitive scattering field distribution and collectively results in broadband transmission anisotropy of the NW lattices (Figure 12(a)). Consequently, a dynamic control over the NW assembly enables switchable optical functionality at the microscale. As the schematic in Figure 12(a) shows, by using a dual electrode design, the authors reversibly rotated the gold NW lattices by 90° on-demand and observed the electric-field controlled transmittance spectra of the assembly systems in the near-infrared region.

Nanosecond laser pulse based optical forces have been used to generate plasmonic nanocomposites with programmable and reconfigurable functionalities.[231,232] Wang, et al. recently have shown that the complex arrangement of silicon NPs in a large size range (from 60 nm to 330
nm) can be achieved by illuminating the NPs with a pulsed nanosecond laser with carefully modulated intensity and polarization. In addition to this, the authors also showed that the material phase of the silicon NPs can be just as well controlled optically by the pulsed laser, which provides an additional degree of freedom to tune the photonic response.

DNA-directed assembly which uses DNA linkers on surfaces of plasmonic NPs for self-assembly configuration control has been regarded as another alternative approach to achieve fine plasmonic tuning. By combining DNA-directed self-assembly with top-down nanofabrication defined templates, Litt, et al. have constructed metasurfaces exhibiting electromagnetically induced transparency (EIT) at near-infrared frequencies, and have demonstrated that the EIT behavior can be dramatically altered in response to chemical stimulus. Figure 12(b) illustrates the fabrication procedure of the proposed metasurfaces. The strategy of lithographically fabricating two parallel NRs and only having a single critical component controlled by the DNA-directed assembly dramatically reduces the possible non-uniformity of the structures, allowing good spectral performance in the near-IR region. By flowing the system with sodium dodecyl sulfate solution and controlling the hydration environment, the authors observed a tunable EIT-like response of the system that was associated with the varying of coupling distance between the fixed NRs and the assembly-controlled components. Using this so-called template-confined DNA-mediated assembly, Lin, et al. have generated a series of uniform arrays of complicated and reconfigurable NP architectures. As depicted in Figure 12(c), the lithography obtained PMMA hole-array structures were comprehensively used to define the planar lattice structure and to control the size and shape of the DNA-functionalized colloidal NPs that are to be assembled in the holes. Figure 12(c) reveals the diversity of the resultant plasmonic NP assemblies obtained using the proposed method incorporated with PMMA hole-array templates of different shape and geometry. Given the extremely high sensitivity of the systems’ optical response to the assembly geometries, the authors demonstrated reconfigurable optical properties including the sample color and absorption spectra enabled by adding EtOH that decreased the gap between NP components in each unit cell.
Figure 12. Directed self-assembly enabled reconfigurable metasurfaces. (a) Au nanowire assembly enabled field switchable broadband polarizers. Schematic of the dual electrode design enabling the rotation of the electric field direction by 90° (top-left). Nanowire suspension in deuterium oxide was contained within an adhesive spacer sandwiched between top and bottom interdigitated gold electrodes. Simulated scattering electric field ($|E_{\text{scat}}|$) distributions of an isolated 1.1-μm-long nanowire for TM and TE excitation at a wavelength of 3.74 μm (top-right). Optical microscope images of nanowire lattices initially assembled and then reconfigured by switching the active electrode for 2.2-μm-long (bottom-left) and 3.7-μm-long (bottom-center) Au nanowires, and the corresponding reconfigurable transmittance spectra (bottom-right). Reproduced with permission.\cite{225}

(b) Hybrid lithographic and DNA-directed assembly showing an EIT-like effect. Schematics of the DNA-directed assembly with (top-left) and without (top-right) e-beam lithography determined trench for spatially selective assembly of the critical components, and the corresponding scattering spectra (bottom). Reproduced with permission.\cite{228}

(c) Template-confined DNA-mediated assembly based superlattices of nanoparticles. SEM images of oriented superlattices consisting of a variety of 1D architectures of gold NPs (top). Optical images of the disk-cube-sphere superlattice with structural features controlled by the EtOH concentration (bottom). Reproduced with permission.\cite{229}

8. Other Materials and Methods

8.1 Aluminum-doped Zinc Oxide (AZO)

Transparent conducting oxides (TCOs) are intensively studied materials which, due to their compatibility with CMOS technology and low-loss dielectric properties, offer great potential for achieving actively controllable metasurfaces. Besides ITO discussed in Section 3, aluminum-doped zinc oxide (AZO) has recently been demonstrated as a novel active material for all-optical response modulation around its ENZ wavelength (~1.3 μm).\cite{233,234} Pump-probe experiments showed that a
modulation time below 1 ps as well as a relative modulation depth up to 40% can be achieved in AZO films obtained from a low-temperature fabrication procedure that controls the defect density. This overcomes the main constraint imposed on the modulation speed of AZO systems, due to the electron-hole recombination time of TCOs being typically ~100 ps.\[^{233}\] A sixfold increase of the Kerr nonlinear refractive index around the ENZ wavelength of AZO has been further identified in thicker (900 nm) films using a shorter pumping wavelength (248 nm).\[^{234}\] Given the similarity of the optical property of ITO and AZO, such as the bandgap, ENZ wavelength, etc., we envision that the hybridization of nanoantennas and AZO may also offer more degrees of freedom in the design of active metasurfaces, including a decrease of required excitation power and flexibility in the linear dispersion engineering, as was recently demonstrated in ITO-plasmonic systems.\[^{120}\] To this end, a systematic comparison between different TCOs in regard to their optical nonlinearity is desired.

As discussed in Section 2, the $\omega_p$ of conducting oxides is primarily determined by their carrier concentration. Previous studies have shown that increased doping level might cause a red-shift of the ENZ wavelength of AZO, because it may increase the mobility of carriers but have less influence on the carrier density.\[^{235}\] Accordingly, AZO films obtained from pulsed laser deposition (PLD) were shown to only support surface plasmons at a wavelength longer than 1.5 $\mu$m due to the limited carrier density. Nevertheless, Kinsey, et al. have recently demonstrated an intrinsic carrier concentration as high as $\sim 10^{21}$ cm$^{-3}$ in AZO, extending the shorter-wavelength edge of AZO's plasmonic response to $\sim 1.3$ $\mu$m.\[^{233}\] It should also be noted that the doping procedure will also vary the electron-hole recombination times in AZO, such as found in heavily-doped silicon through Auger processes, although these may be accompanied by an increase in undesired thermal effects.

8.2 Magnesium (Mg) and Palladium (Pd)

As summarized in a recent review paper,\[^{236}\] beyond the noble metals such as silver and gold that have been widely used in nanooptics, alternative materials that can support plasmonic resonance have been recently studied. Among these materials, magnesium (Mg)\[^{41,237–240}\] and palladium (Pd)\[^{42,241,242}\] have been intensively investigated due to their tremendously attractive material characteristics that can be exploited to enabling reconfigurable metasurfaces.

The dynamic plasmonic response of Mg nanostructures originates from the following two properties. First, when Mg nanostructures are put in a hydrogen environment, Mg undergoes a metal-to-dielectric transition to become magnesium hydride (MgH$_2$). While generally slow, this process is reversible when Mg is then exposed to oxygen. Second, Mg is a novel material for plasmonics in the visible range, while MgH$_2$ is dielectric. Consequently, active properties, such as
scattering, chirality and plasmonic color of Mg metasurfaces can be achieved via controlling the gaseous environment. It is worth noting that, in order to facilitate the hydrogenation/dehydrogenation process, a palladium (Pd) capping layer of a few-nanometers-thick has been usually introduced on top of the Mg nanostructures, separated by a thin titanium (Ti) spacer. The Pd layer catalyzes the splitting of molecular H\textsubscript{2} into single hydrogen atoms which diffuse through the Ti spacer into the Mg lattice. The Ti layer has been used as a buffer layer for two purposes: to release the mechanical stress between Pd and Mg and to suppress the alloying tendency of the two metals. In the context of hydrogen economy, the plasmonic properties of Mg that can absorb up 7.6 wt % of hydrogen gas are of particular interest to researchers in both fields of optics and sustainable energy. To gain a deeper understanding of the switchable behavior of Mg nanostructures upon absorption of hydrogen gas, Sterl et al. have recently developed a novel method to visualize the hydrogenation process in an individual nanoparticle, called nanoscale hydrogenography, by combining three techniques: near-field scattering microscopy, atomic force microscopy, and single-particle far-field spectroscopy. The information obtained from this method provides a comprehensive picture of the evolution of the hydrogenation process in a single nanoparticle, in which the nanocrystalline structure determines the temporal property of the Mg to MgH\textsubscript{2} phase transition. Besides the hydrogenation process, Mg metasurfaces actually offer a novel platform for exploring reconfigurable plasmonics based on many other chemical reactions owing to Mg’s relatively active chemical characteristics. Taking advantage of the fact that Mg is a dissolvable conductor, Li et al. recently reported Mg metasurfaces for indirect nanoplasmonic environmental and biomedical sensing in the visible region. Experiments showed that, besides the detection of ambient conditions, the humidity-sensitive optical response of Mg metasurfaces fabricated on top of flexible nanoengineered polyurethane templates can be extended to monitor physiological processes, such as physical activities, by sensing sweating on the skin.

It should be noted that the Mg-MgH\textsubscript{2} phase transition is an intrinsically slow dynamic process due to the dissociation process of hydrogen molecules and the volumetric diffusion of hydrogen atoms in the Mg structures, leading to the relevant plasmonic modulations on a minute time-scale. Moreover, due to the high thermodynamic stability of MgH\textsubscript{2}, the corresponding dehydrogenation process associated with the reverse plasmonic resonance switching generally takes a longer time. To enable Mg based active plasmonics with better temporal performance, future work may focus on optimization of two factors: (i) the catalytic process of hydrogen dissociation and (ii) nanostructures with a reduced diffusion time of hydrogen atoms.
One of the primary motivations for Mg and Pd metasurfaces is their potential for the development of plasmonic hydrogen sensors that may provide remote readout of hydrogen concentration. Despite the superior plasmonic properties (lower optical loss, etc.) of Mg in the visible region, Pd (and Pd-alloy) based metasurfaces have been shown to be promising for hydrogen detection of faster dynamics in the low pressure regime.\cite{241,242} Moreover, the intrinsic hysteresis behavior observed in Pd’s plasmonic response offers more information about its reconfigurability, which can potentially be used for a plasmonic memory effect. By fabricating Pd and Pd-Au alloyed nanohelix structures, Matuschek et al. recently have demonstrated that, compared with the standard extinction spectroscopy, chiroptical responses of the metasurfaces can be used to realize highly sensitive hydrogen sensing with good linearity.\cite{42}

8.3 Electrochemical Method

Electrochemical processes in general refer to the class of phenomena which simultaneously involve both chemical and electrical effects. Particularly, chemical changes due to electrochemical reactions offer a unique approach for electrically controllable plasmonics that are sensitive to the chemical constituent and the surface carrier properties of the nanostructures. Electrochemical potential controlled plasmonic devices have recently been reported and should prove useful for active and fine tuning of plasmonic properties of metallic metasurfaces.\cite{243–250} Dramatic plasmonic resonance tuning based on surface-charge density modulation was first observed in arrays consisting of 10-nm thick gold SRR\cite{243} and has been recently reidentified in gold nanoporous systems with remarkable surface-to-volume ratios.\cite{248} Moreover, electrochemical processes can also directly result in changes in constituent material properties, which may lead to dramatic variation in the associated plasmonic response. Harnessing the Ag-AgCl redox chemical reaction, Byers et al. have demonstrated a reversibly tunable resonance of silver based plasmonic nanoparticles.\cite{246} Similarly, by electrochemically controlling the structure of nanoantennas through metal dissolution, Minamimoto et al. recently have reported fine tuning of the plasmonic behavior of gold nanodisk arrays.\cite{250} Wang et al. have demonstrated real-time color control of plasmonic metasurfaces based on the combination of bimetallic nanodot arrays and electrochemical bias.\cite{247} Moreover, an electrochemical potential controlled strong coupling effect has also been identified in active metasurface systems composed of gold-nanoantennas and redox-state-tuned dye molecules.\cite{249} This study revealed that the energy of electrons in gold nanostructures and the redox state of the dye molecules can be simultaneously tuned by electrochemical potential, resulting in actively controlled strong coupling states between localized surface plasmons (LSPs) and molecule excitons.

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It should be noted that despite its obvious advantages discussed in these studies, such as CMOS compatibility and broad tuning capability, electrochemical methods in general are slow processes. Therefore, electrochemical tunable metasurfaces are suitable for plasmonic systems exhibiting reversibly and precisely tuned responses.

9. Conclusions and Outlook

Nanoengineering of active materials and plasmonic structures constitutes a powerful approach to building active metasurfaces that are of high interest in the realization of metadevices for optical information processing, display and storage. The ultra-thin characteristics and resonant nature of metasurfaces dramatically boost the influence of active materials possessing variable optical properties, which has resulted in a variety of highly tunable metasurfaces as well as a deeper understanding of light-matter interaction on a nanometer scale. Recent years have witnessed the development of active metasurfaces toward faster, stronger and more accurate tuning, which in turn has brought major progress in the studies and understandings of optically interesting materials and their integration with nanostructured photonic architectures. Nevertheless, in order to meet the needs of practical devices, more work is required to further improve the performance of metadevices. Fortunately, the explosive development of nanotechnology that continues to shed new light on the synthesis and fabrication of nanomaterials offers an unprecedented opportunity to explore tunable and reconfigurable artificial materials based on new tuning mechanisms. The literature is replete with examples of these developments. For instance, the recent success in synthesis of large-area monolayer two-dimensional transition-metal dichalcogenides (2D TMDCs) and in their integration with metallic nanostructures can potentially enhance metadevices with strain-induced tunable nonlinearities. The steady development of 3D printing technology that has made it possible to create complex structures with feature dimensions at micro- or even nanometer scale may provide the foundation for new design concepts based on mechanically-induced photonic tuning. Furthermore, recently reported hybrid plasmonic systems exhibiting strong coupling between plasmons and excitons in, for example, organic semiconductors are expected to enable all-optically tunable photonics, indicating the potential of metasurfaces as platforms for active quantum plasmonics. To this end, we hope that this Report will give some inspiration not only for better understanding of the recent development of active optical metasurfaces, but also for the future efforts in this research area.

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Conflict of Interest

The authors declare no conflict of interest.

References


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Optical metasurfaces provide unprecedented flexibility in tailoring light-matter interactions on subwavelength scales, while their dynamic responses are critical for the development of practical metadevices. Here the authors review the recent advances in active optical metasurfaces, highlighting a group of active materials, including phase change materials (GeSbTe and VO$_2$), indium tin oxide, graphene, liquid crystals, semiconductors, etc., and also other emergent approaches.