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Plasmonic semiconductors: materials, tunability and applications

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ABSTRACT

Semiconductor plasmonics has become a frontier for light manipulation beyond the diffraction limit, offering a broader spectral range and higher flexibility of plasmon resonances. Due to versatile and unique plasmonic properties, semiconductor nanostructures hold high promise in a plethora of applications, such as integrated photonics, solar energy, and biosciences. This review discusses the advances in semiconductor plasmonics, establishing links among the distinctive nanostructures, tailorable plasmon properties, and ever-expanding applications. It sheds light on the characters and dynamics of plasmons in semiconductors throughout their lifetime. The review then showcases representative plasmonic semiconductor swhile sketching a roadmap on tailoring plasmonic response in semiconductor platforms spanning nanocrystals, metasurfaces and heterostructures. Next, the overview of plasmonic semiconductor applications highlights the relevance of pronounced plasmon resonance with mitigated loss and the utilization of damping-induced hot carriers and thermalization. Finally, we conclude by envisioning the prospects and challenges of this field.

1. Introduction

The wave nature of light imposes a diffraction limit, defined as the critical distance between two distinguishable points on the order of λ/n , where λ and n are the incident wavelength and the refractive index of the medium, respectively [1,2]. To overcome this diffraction limit is of tremendous scientific and technological interest. It facilitates reaching subwavelength imaging resolution and miniaturizing the footprint of optical devices. The advent of plasmonics echoes this call. Surface plasmons, resulting from the interaction of oscillating free carriers in matter with incident electromagnetic fields, allow extreme light confinement and near-field enhancement at nanometric dimensions on the sub-femtosecond (fs) timescale [3]. Surface plasmons can be propagating surface plasmon-polaritons when excited on and propagating along a planar metallic-dielectric interface, while denoted as localized surface plasmon resonance (LSPR) when excited and confined in the vicinity of nanoparticles. Subsequently, throughout the lifetime of surface plasmons, a multitude of plasmonic effects emerge, including hot-carrier generation and transfer, local plasmonic thermalization, collective plasmon resonances, and coupling of plasmonic modes with neighboring resonances or external fields.

Classical host materials for plasmons are mostly metals, especially Au and Ag, which possess the key merits of strong plasmon resonance, high conductivity, and synthetic accessibility [4,5]. In recent decades, plasmonic semiconductors have also come into play, complementing metals. The inherent plasmonic bands in semiconductors, typically in the regime from the near-infrared (NIR)-to-

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Received 27 March 2023; Received in revised form 2 June 2023; Accepted 26 June 2023 Available online 27 June 2023 0079-6425/© 2023 Elsevier Ltd. All rights reserved. terahertz (THz) frequencies, expand the spectral region not covered by metals. These plasmonic bands spectrally overlap with the telecommunications bands (1260–1625 nm), solar energy spectrum (295–2500 nm), and biological transparency window (650–1350 nm). Furthermore, the material diversity in the semiconductor family renders their functional versatility. Thus, semiconductors exhibit unique plasmon kinetics and plasmonic phenomena that breed new fields, including plasmontronics, quantum plasmonics, plasmon valleytronics, programmable plasmonics, and plasmonic twistronics, amongst others. Notably, the plasmonic properties of semiconductors are tailorable to an unrivaled extent by a wealth of *in-situ* factors and post-synthetic approaches, as depicted in Fig. 1a. Plasmonic semiconductors, therefore, offer tempting opportunities for ever-expanding applications, as shown in Fig. 1b. Some applications take advantage of the pronounced near-field enhancement with mitigated losses, while others utilize the hot carriers and thermalization induced by plasmon damping. The practical use of plasmonic semiconductors also profits from their virtues of source abundance, easier processability, and the complementary metal–oxide–semiconductor (CMOS) compatibility [6–13].

This Review surveys the advances in semiconductor plasmonics, covering a wide range of material and nanostructure systems. First, it sheds light on the up-to-date and in-depth theoretical developments in semiconductor plasmonics while sketching a roadmap for plasmon tuning strategies in reproducible, dynamic, and reversible manners. The progress, as mentioned above, is further interlinked with plasmonic applications where semiconductors possess unique strengths.

The Review is organized as follows: In Section 2, we interpret the physics of plasmonic modes, plasmon coupling, and plasmon dynamics during excitation, decay, relaxation, and energy transfer. We also overview technological developments in plasmon characterization. Section 3 outlines representative plasmonic semiconductor materials. Along with classical conductive metal oxides, metal chalcogenides, refractory nitrides, and III–V semiconductors, we highlight emerging candidates, including two-dimensional van der Waals (2D vdW) materials and phase-change materials. Section 4 provides an exhaustive overview of plasmonic tailoring strategies in semiconductor nanocrystals, metasurfaces, and heterostructures. In Section 5, we elaborate on the applications of plasmonic semiconductors, mainly focusing on integrated photonics, solar energy, and biosensing. The discussion concentrates on the link between plasmon dynamics and tunability as the basis for their functional versatility. Finally, Section 6 concludes the review with an outlook on developing trends, emerging subdisciplines, and remaining challenges in semiconductor plasmonics.

2. Plasmonics in semiconductors

2.1. Plasmon resonance in semiconductors

2.1.1. Plasmon polaritons

2.1.1.1. Propagating surface plasmon polaritons (SPPs). Propagating SPPs are excited when an incident electromagnetic wave coherently oscillates with free carriers at a metallic-dielectric interface. Thus, SPPs form a transverse-magnetic (TM) wave propagating along the metallic-dielectric interface but evanescent in the normal direction, as shown in Fig. 2a. Under the assumption of an infinite flat metal-dielectric interface, the SPP dispersion relation, relating its in-plane wavevector to its frequency, is expressed as [14,15]:



Fig. 1. Plasmon tunability, mechanisms and applications in highly doped semiconductors. (a) Typical approaches to plasmon tailoring in semiconductor nanocrystals, heterostructures, and metasurfaces. (b) Primary plasmonic effects in propagating surface plasmon polaritons (SPPs) and localized surface plasmons (LSPs). Applications of plasmonic semiconductors governed by the corresponding plasmonic effects.

(2)

$$k_{\parallel} = k_0 \sqrt{\frac{\varepsilon(\omega)\varepsilon_d}{\varepsilon(\omega) + \varepsilon_d}},\tag{1}$$

$$k_{\perp}^2 + k_{\parallel}^2 = \varepsilon_d k_0^2,$$

where $k_0 = \omega_p/c$, c being the speed of light. ω_p is the bulk plasma frequency [16]. $\varepsilon(\omega)$ and ε_d represent the permittivity of the plasmonic and surrounding materials, respectively. $k_{||}$ and k_{\perp} are the SPP wavevector components parallel and normal to the conductive surface, respectively. Hence, a surface plasmon resonance occurs when $\varepsilon(\omega) + \varepsilon_d = 0$, yielding $Im\{k_{\perp}\} \gg \varepsilon_d^{1/2}k_0$ where $Im\{k_{\perp}\}$ is the imaginary part of k_{\perp} . Therefore, the SPP mode decays exponentially with distance from the interface, resulting in extreme light confinement that overcomes the diffraction limit. As depicted in Fig. 2b, the electromagnetic field of an SPP penetrates in the dielectric medium deeper than in the conductive medium. This senario becomes more prominent under incident light of longer wavelengths [17–19]. In contrast, along the metallic-dielectric interface, SPPs can propagate for hundreds of micrometers. This propagating nature allows SPPs to be excited or detected remotely, avoiding direct laser irradiation on the measured sample [15,20].



Fig. 2. Plasmon polariton character. (a) SPP electromagnetic waves excited by a classical Kretschmann prism and propagating along the metallicdielectric interface. Reproduced with permission [15]. Copyright 2019, De Gruyter. (b) Penetration profile of the SPP wave into the dielectric and conductive media. Reproduced with permission [15]. Copyright 2019, De Gruyter. (c) Localized surface plasmons excited from the resonance interaction between the oscillating electron cloud in the nanoparticles and the incoming light. Reproduced with permission [353]. Copyright 2020, Wiley-VCH. (d) Simulated localized surface plasmon resonance in indium-tin-oxide (ITO). The absorption spectra with the line-shape asymmetries show the plasmonic response and damping under different frequencies, in which Γ_L and Γ_H are the low-frequency and high-frequency damping constants, respectively. Reproduced with permission [29]. Copyright 2014, American Chemical Society. (e) Simulation of electromagnetic field enhancement ($|(E/E_0)|^2$) at hot spots within gaps of different nanoantenna configurations. Reproduced with permission [353]. Copyright 2020, Wiley-VCH. (f) Excitation of the cyclotron magnetoplasmonic mode in a semiconductor nanoparticle when applying a magnetic field with both leftand right-handed circular polarization (LCP and RCP). Reproduced with permission [75]. Copyright 2018, Springer Nature. (g) Magnetic circular dichroism (MCD) spectra of Mo-doped In₂O₃ nanocrystals collected at 1–7 T magnetic field strengths. Reproduced with permission [75]. Copyright 2018, Springer Nature.

(11)

2.1.1.2. Localized surface plasmons. When launching plasmon polaritons in a nanoparticle, LSPR can be understood as the oscillating collective displacement of electrons against the matrix of atomic cores, as shown in Fig. 2c [21]. This dipolar or multipolar resonance causes an extinction maximum. The polarizability a_p describes the ratio of the induced dipole moment in a nanoparticle (**p**) to the incident electromagnetic field **E**, expressed as $\mathbf{p} = a_p \varepsilon_0 \varepsilon_d \mathbf{E}$. Under the Rayleigh (electrostatic) approximation, where the particle radius *R* is significantly smaller than the incident light wavelength λ , a_p in a spherical particle is expressed as [22]:

$$\alpha_p = 4\pi R^3 \frac{\varepsilon(\omega) - \varepsilon_d}{\varepsilon(\omega) + 2\varepsilon_d},\tag{3}$$

where ε_0 is the vacuum permittivity. Hence, a localized resonance occurs when $\varepsilon(\omega) + 2\varepsilon_d = 0$. The extinction cross-section (σ_{ext}) also quantifies the interaction of light with a particle, which is described under the electrostatic approximation as [22]:

$$\sigma_{ext} = \sqrt{\varepsilon_d} k_0 Im\{\alpha_p\} = 4\pi R^2 \left[k_0 \sqrt{\varepsilon_d} R \right] Im\left\{ \frac{\varepsilon(\omega) - \varepsilon_d}{\varepsilon(\omega) + 2\varepsilon_d} \right\} = \sigma_{sca} + \sigma_{abs}.$$
(4)

Therefore, σ_{ext} is a measure of the effective area of the electromagnetic field when interacting with the nanoparticle, which is the sum of its absorption and scattering cross-section.

For a spherical particle of arbitrary size and material, the electromagnetic field distribution under incident light, along with σ_{ext} , can be analytically solved using Mie theory. Mie theory correlates the amplitude of the scattered electric field E_s with that of the incident field E_i to the amplitude scattering matrix $\begin{bmatrix} S_2 & 0 \\ 0 & S_1 \end{bmatrix}$, as given by [22,23]:

$$\begin{bmatrix} E_{\parallel s} \\ E_{\perp s} \end{bmatrix} = \frac{e^{ik(r-z)}}{-ikr} \begin{bmatrix} S_2 & 0 \\ 0 & S_1 \end{bmatrix} \begin{bmatrix} E_{\parallel i} \\ E_{\perp i} \end{bmatrix}.$$
(5)

Thus, Mie theory reveals the net electrical fields outside (E_{out}) and inside (E_{in}) the spherical particle as:

$$E_{out}(x, y, z) = E_0 \hat{z} - \left[\frac{\varepsilon(\omega) - \varepsilon_d}{\varepsilon(\omega) + 2\varepsilon_d}\right] R^3 E_0 \left[\frac{\hat{z}}{r^3} - \frac{3z}{r^5} (x\hat{x} + y\hat{y} + z\hat{z})\right]$$
(6)

$$E_{in}(x, y, z) = \left[\frac{3\varepsilon(\omega)}{\varepsilon(\omega) + 3\varepsilon_d}\right] E_0 \hat{z},\tag{7}$$

where E_0 is the incident electric field magnitude; r is the distance from the particle center; x, y and z are the position from the particle center, with \hat{x} , \hat{y} , \hat{z} being the unit vectors of corresponding spatial coordinates. For particles of more complex shapes, the LSPR field simulation should resort to more advanced computational techniques to obtain a numerical solution to Maxwell's equations [24]. According to simulations and experimental observations, the light confinement induced by LSPR can remarkably enhances the near field by a factor of 10^4 – 10^6 . In addition, the spacial distribution of free carriers or dopants in a plasmonic nanostructure leads to a substantial local field increase exceeding 10^{14} times in so-called "hotspots" [25–27]. Hotspots tend to appear at the edges and corners of nanostructure, and in the gaps of aggregates.

2.1.2. Fundamentals of plasmon resonances in semiconductors

2.1.2.1. General description: The Drude model. The Drude model is widely applicable to interpreting the optical response of a plasmonic platform. It describes its dielectric function and is valid under two assumptions: (i) non-interacting motion of free carriers and (ii) only instantaneous collisions between moving carriers and the nuclei lattice. The Drude model can be expressed as:

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) = \varepsilon_{\infty} - \frac{\omega_p^2}{\omega(\omega + i\gamma)},$$
(8)

where $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are the real and imaginary parts of the dielectric constant, respectively. ε_{∞} is the material's dielectric constant at high frequencies, which takes into account the polarization effect of the ion core background. γ is a damping constant also known as the collision or scattering frequency). From Equation (8), $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ can be deduced as:

$$\varepsilon_1(\omega) = \varepsilon_{\infty} - \frac{\omega_p^2}{\omega^2 + \gamma^2} \tag{9}$$

$$\varepsilon_2(\omega) = \frac{\omega_p^2 \gamma}{\omega(\omega^2 + \gamma^2)}.$$
(10)

According to equation (1) and (3), resonant interaction occurs when $\varepsilon_I(\omega)$ is negative in the plasmonic materials. The imaginary part $\varepsilon_2(\omega)$ accounts for the scattering and decay of surface plasmons during free-carrier motion [28]. Furthermore, ω_p and γ can be calculated from:

$$\omega_p{}^2 = \frac{ne^2}{\varepsilon_0 m^*}$$

$$\gamma = e/(\mu m^*),\tag{12}$$

where *n* is the free carrier density, *e* is the elementary electronic charge, and m^* is the carrier effective mass [28,29]. Hence, a high free-carrier density is essential in sustaining a metallic conductivity and plasmonic response [24]. γ is associated with damping induced by scattering events, including (i) electron–phonon scattering, (ii) electron–electron (hole-hole) scattering, (iii) interband transitions, (iv) surface scattering, and (v) ionized impurity scattering [29,30]. The intraband transitions are critical for the lossy nature of metals, while the ionized impurity scattering is indispensable for damping in semiconductors [16]. A viable way to suppress the optical loss is to tune the plasmon frequency spectrally away from the energy of certain dominant scattering events [31].

Fig. 2d depicts typical extinction spectra of plasmon resonances. ω_p governs resonance bands' position, while γ and background permittivity determine the width and shape, respectively. The full width at half-maximum (*FWHM*) is a common trait indicating the peak width, while the quality factor (Q-factor) is the ratio between ω_p and *FWHM*. Q-factor considers the impacts of both μ and n, described as [5,6,29,32]:

$$Q = \frac{\omega_p}{FWHM} = \frac{\omega(\frac{d\epsilon_1}{d\omega})}{2\epsilon_2}.$$
(13)

2.1.2.2. Plasmon resonances in semiconductors. When discussing plasmonic response in highly doped semiconductors, one should also take into account of electronic interband transitions, especially when the energy of incoming photons surpasses the bandgap. The Lorentz-Drude model should thus be considered, which gives a better fit to experimental data:

$$\varepsilon(\omega) = \frac{\Delta \varepsilon \Omega_p^2}{\Omega_p^2 - \omega^2 - i\Gamma\omega}$$
(14)

where Ω_p , Γ and $\Delta \varepsilon$ are the plasma frequency, the damping constant and a parameter weighing the impact of an interband transition on the dielectric constant, respectively. The LSPR behavior in semiconductors is most widely investigated in semiconductor nanocrystals, which are colloidally synthesized crystalline nanoparticles.

Surface plasmons behave differently in semiconductors than in metals. The majority carriers in semiconductors, electrons and holes, could launch plasmon polaritons, while they are only excited by electrons in metals. The free-carrier densities in plasmonic semiconductors are typically in the 10^{18} – 10^{21} cm⁻³ range, several orders of magnitude lower than in metals (10^{23} cm⁻³) [29,33]. Hence, surface plasmon frequencies cover a much broader spectral range in semiconductors, spanning from near-infrared (NIR) to terahertz (THz) wavelengths [14,34,35].

Plasmon resonances dampen mostly by impurity scattering in semiconductors, resulting in broader and asymmetric plasmonic bands. The spectral asymmetry is attributed to the screening of scattering centers at high frequency, which is highly dependent on ε_{∞} [29,36]. For instance, in Sn-doped In₂O₃ (indium tin oxide, ITO) with a relatively low ε_{∞} ($\varepsilon_{\infty} = 4$), ionized Sn dopants are effectively screened by the electron cloud in the lower frequency range of $\omega' < \omega_p$. Thus, the electron cloud coherently responds to the local field fluctuation, imposing a profound damping of plasmonic response. In the high-frequency region of $\omega' equat \ge \omega_p$, the electron cloud may not oscillate coherently to the local field. Thus, the ionized Sn behaves purely as Coulomb scattering centers. The breakdown of this effect endows the whole system with a reduced scattering probability [37–40]. Due to this damping anisotropy, the extinction band exhibits apparent spectral asymmetry. As shown in Fig. 2d, this asymmetry becomes more pronounced in semiconductors with a significant crossover frequency $\Gamma_X = \Gamma_L - \Gamma_H$, where Γ_L and Γ_H are the low-frequency and high-frequency damping constants, respectively. In contrast, semiconductors with high ε_{∞} , such as Cu_{2-x}Se ($\varepsilon_{\infty} = 10$), have an asymmetric plasmonic band due to ω_p -independent damping [41].

2.1.3. Plasmon coupling in semiconductors

2.1.3.1. Coupling between plasmonic modes. A plasmonic mode forms via collective electron oscillation, creating an electromagnetic field extending within and outside the plasmonic structure. Hence, mode coupling can occur in neighboring plasmonic nanostructures when their evanescent fields overlap. Plasmonic coupling can remarkably amplify the plasmon resonances and even boost SPP propagation. One typical scenario is plasmon coupling in metasurfaces, which are arrays of plasmonic nanostructures of sub-wavelength dimensions and pitches. Each nano-unit in the metasurface, known as a nanoantenna, acts as a plasmonic resonator when subjected to an electromagnetic field. Depending on the surface charge distribution, a plasmonic nanoantenna could excite a dipole, a quadrupole or a high-order multipole. In addition, the gaps between nanoantennas accommodate hotspots, providing local field enhancement over 10^5 -fold, as illustrated in Fig. 2e. These hotspots raised considerable interest for Raman signal amplification in surface-enhanced Raman spectroscopy (SERS) [1,17,24,42–45]. The spectral characteristics of plasmon resonances are highly susceptible to the metasurface geometry. Owing to inherently lower plasmon energies in semiconductors, their metasurfaces provide additional knobs to extend the plasmonic response towards the mid-infrared (MIR) range, manipulating the plasmon distribution and propagation [11,46–48]. We will elaborate on plasmon tailoring in semiconductor metasurfaces in Section 4.2.

Plasmon hybridization is another means of inter-plasmon interaction, as interpreted by the hybridization theory [14,15,49,50]. This theory considers each lowest-order plasmonic mode as a harmonic mass-spring system. The inter-mode interaction causes mode splitting and, eventually, gives rise to multiple-mode excitation [16]. Hence, plasmon hybridization in semiconductors results in a remarkable broadening of plasmonic response, as well as efficient heat-flux exchange by plasmonic thermalization, as will be discussed

in Section 4.1 [10,51].

2.1.3.2. Coupling between plasmonic and other modes. The coupling of plasmonic and excitonic modes launches plasmon-exciton polaritons, triggering a wealth of optical phenomena [16,52–54]. Excitons in an emitter can generate surface plasmons via energy transfer to the adjacent plasmonic nanostructures. In a reverse process, surface plasmons can significantly amplify the radiation from the nearby emitter via collective oscillations of surface carriers. Moreover, plasmon-exciton coupling provides further control of the emitted light, providing effective manipulation over its intensity, directionality, radiation modes, decay rate and quantum efficiency [55–57]. Plasmon-exciton polaritons also serve as energy-exchange intermediaries for the ultralong-distance energy transfer of excitons [20,53]. Plasmon-exciton polaritons in an optical cavity further reinforce emission enhancement and control without crosstalk, and can produce direction-selective polariton propagation [58]. Plasmon-exciton coupling in semiconductor nanostructures is particularly enticing for infrared light emission, which opens new gateways for single-photon detection, non-linear quantum optics, on-chip broadband couplers, all-optical logic gates, polarization-dependent beam splitters, and low-threshold lasers [16,27,59–65]. In recent years, plasmon-exciton interaction under circularly polarized light has aroused much interest to enable efficient control of chiral photon emission [66], and engineer the transmitted-light wavefront in tunable metasurfaces [67].

Plasmonic modes can also couple to phonon modes and molecular vibrations of native ligands, which excites collective resonance and new functionality [68,69]. Plasmonic-phonon coupling forms hybrid interface polaritons in the SiO₂/black phosphorus/SiO₂ heterostructure. This plasmonic system underpins femtosecond optical switching [70]. Rajapitamahuni *et al.* modulated the plasmon–phonon coupling in β -Ga₂O₃ films via electrostatic doping, which leads to a dynamic change in the film mobility and electron–phonon interactions [71]. Agrawal *et al.* discovered a Fano mode in Sn-SPS:name::sbnd and F-SPS:name::sbnd co-doped In₂O₃ (Sn,F: In₂O₃) nanocrystals, which arises from the coupling between LSPs and the C–H vibration of oleate ligands. The optical decay rate of absorption, transmission, and reflection governs the Fano mode [72].

2.1.3.3. Plasmon interactions with external perturbations. Along with a diversity of plasmonic mode coupling, plasmonic semiconductors are also susceptible to external electrical, magnetic, and thermal fields. An external electric field perturbs the plasmon resonances by means of electrostatic doping, carrier density fluctuations, charged impurity scattering, or electrical channel tunneling [60,61,73]. Alternatively, an external thermal gradient changes the plasmon frequency in semiconductors by varying the free-carrier concentration [74]; for instance, thermal treatment alters the THz plasmonic response in InSb arrays [24]. An external magnetic field allows carrier-polarization manipulation through plasmon-spin interaction in plasmonic semiconductors including Sn-doped In₂O₃ (ITO), Mo-doped In₂O₃, self-doped TiO₂, InN, and Cu_{2-x}Se. It opens up the discipline called *plasmontronics* [75–77]. As schematically illustrated in Fig. 2f, the intrinsic plasmon-exciton coupling excites the cyclotron magnetoplasmonic modes and subsequent Zeeman splitting of excitonic states in Mo-doped In₂O₃ nanocrystals, leading to selective carrier polarization via spin–orbit coupling [75]. As



Fig. 3. Plasmon excitation, decay, energy dissipation and transfer in a plasmonic nanoparticle. CID denotes chemical interface damping, while DICTT and PICTT represent direct and plasmon-induced interfacial charge transfer transition, respectively. Only one condition of band alignment and interface band offset is sketched for indication.

governed by intrinsic plasmon-exciton and plasmon-spin interactions, the electron polarization is controlled by the irradiation of left circularly polarized (LCP) or right circularly polarized (RCP) light under a magnetic field. The MCD spectra in Fig. 2g, as a measure of the difference in absorption of LCP and RCP light, show a linear correlation between the MCD intensity and the magnetic field, verifying the plasmonic coupling.

2.2. Plasmon kinetics in semiconductors

The primary kinetic processes throughout the lifetime of a plasmon, as depicted in Fig. 3, encompass (i) plasmon excitation, (ii) radiative decay, (iii) Landau damping for hot carrier generation, (iv) hot carrier relaxation and transfer, and (iv) local thermalization. Following this sequence, this subsection will sketch the plasmon dynamics in different plasmonic platforms, in which highly doped semiconductor nanostructures are particularly highlighted.

2.2.1. Surface plasmon excitation

Direct light radiation is the most common way to launch surface plasmons at a metallic-dielectric interface, which entails an additional setup to fulfill the momentum-matching conditions, for example, a high-refractive-index glass prism, a nanoantenna, or grating structures [14,78]. Fig. 2a depicts a classical Kretschmann configuration for SPP excitation. On the other hand, LSPs can be excited without the constraint on the incident angle. Therefore, they are beneficial for device scaling. In the last decade, a rich set of photon sources for surface plasmon excitation have been developed, mainly including the light in the waveguide, emitters, and single-photon sources [16,79]. Among them, single-photon emitters can produce single quantized plasmons, tantalizing for optical quantum information applications.

Electrical pumping has become an intriguing route to excite surface plasmons, primarily by employing a high-energy local electric field or electron quantum tunneling. The prior strategy requires irradiating a focused electron beam on plasmonic structures. Under the Coulomb interaction, free carriers in the plasmon host collectively oscillate with the incoming electromagnetic field to excite surface



Fig. 4. Excitation and characterization of surface plasmons. (a) Scanning near-field microscopy (SNOM) intensity profile of a monoclinic metallic VO_2 nanostripe. × represents the distance on the nanostripe from the edge of the Au electrode. Inset: SNOM image of the VO_2 stripe. Scale bar: 5 µm. Reproduced with permission [117]. Copyright 2020, American Chemical Society. (b) Electrically-activated excitation of surface plasmons between the two arms of a V-shaped Au nanoantenna. Inset image: electroluminescence spot of spontaneously emitted light. Reproduced with permission [60]. Copyright 2017, American Chemical Society. (c) Back focal plane image of a V-antenna under an applied voltage of 2 V, with a directivity of +1.3 dB in the directional radiation pattern. Reproduced with permission [60]. Copyright 2017, American Chemical Society. (d) Electron energy-loss spectroscopy (EELS) spectra and (e) fitted EELS intensity maps of plasmonic MoO₂ nanoribbons on Si₃N₄ membrane. Reproduced with permission [118]. Copyright 2020, Wiley-VCH.

plasmons. Tip-scanning techniques also increase the efficiency of plasmon excitation, which appreciably amplifies the near-field at the tip-surface interaction point. Schrecongost *et al.* created plasmonic patterns on a thin VO₂ film by scanning a biased atomic force microscopy (AFM) probe, as illustrated in Fig. 4a.⁴² This method allows flexible modulation of free-carrier density on VO₂, enabling stable and reversible guidance and modulation of plasmons.

Electron tunneling can excite plasmon polaritons by inelastic scattering of electrons, which travel across the tunneling junction (nanoantennas) under bias. The two-wire architecture is the most popular tunnel channel configuration, where efficient electrical energy transfer at the feed point triggers the plasmon resonance. However, this geometry lacks rational control over the radiation direction of plasmon polaritons. One approach to address this issue is to design an antenna geometry with broken rotational symmetry [52]. Fig. 4b showcases an in-plane tunneling V-antenna sustaining quadrupole-like plasmonic modes under biasing [60]. This asymmetric two-arm structure supports the flexible modulation of plasmon population and directivity. Within the tunnel junction, there is a broad spectral overlap between the fundamental antenna resonance and the dipole emission. The interference ensures light emission with high directivity, tunability, and efficiency. As shown in Fig. 4c. The electrical excitation of plasmon polaritons bridges the gap between electronics and optics, paving the way for plasmonic integrated circuits.

2.2.2. Hot-carrier generation and transfer

The plasmon resonance starts to damp right after photoexcitation with fs timescale. Apart from radiative decay, plasmons also decay non-radiatively to form hot carriers with substantially higher temperatures than thermally excited carriers (up to thousands of K). This hot carrier generation process is known as Landau damping [27,80,81]. Landau damping occurs within 1–100 fs of delay time from the creation of surface plasmons and typically in <10 fs in semiconductors [8,81,82]. Hot carriers then undergo relaxation to redistribute their energy and radiate heat to the environment, involving electron–electron/hole-hole scattering (100 fs–1 ps after plasmon excitation), electron/hole-phone scattering (1–10 ps) and phonon–phonon scattering (10 ps–10 ns). Charge recombination and trapping are other nonnegligible processes during plasmon damping, occurring within a ps delay timescale from hot-carrier generation [83]. Notably, hot carriers induced by plasmons survive much longer in nanoparticles than on an extended surface, ascribed to the synergies of (i) the field confinement, (ii) a higher density of states, and (iii) suppressed electron–electron or electron–phonon interaction in nanoparticles [84,85]. Therefore, studies of hot carriers are mostly carried out in plasmonic nanostructures.

Nevertheless, ultrafast hot-carrier relaxation and charge recombination impose major obstacles to the practical utilization of the superior light-harvesting capabilities of plasmonic nanostructures. A remedy to this issue is injecting hot carriers into a nearby absorbate or semiconductor to maintain their energetic nature while sustaining a long-lived, nonlocal spatial distribution [86,87]. The transfer pathways of hot carriers, as depicted in Fig. 3, lay the foundation for regulating interfacial hot carrier dynamics to improve performance in plasmonic devices [88,89]. In plasmonic semiconductors, hot carriers transfer across the interface through either indirect or direct pathways. In the indirect transfer process, taking hot electrons as an example, they initially form in the plasmonic nanostructures, then traverse into a nearby absorbate or semiconductor. The process occurs when their energies surpass the lowest-unoccupied-molecular-orbital (LUMO) of the absorbate or the conduction band minimum (CBM) of the adjacent semiconductor [78]. By contrast, the direct transfer process occurs during plasmon dephasing, requiring strong hybridization between the plasmonic nanocrystal and absorbate/semiconductor to form interfacial states.

To date, the study of the indirect transfer path prevails, as generally gauged by the transfer efficiency and lifetime of charge separation. The transfer efficiency can be described by Fowler's law: [90,91]

$$\eta_i = C_F \frac{(h\nu - e\Phi_B)^n}{h\nu} \tag{15}$$

where η_i is the injection rate of hot carriers; C_F is the Fowler emission coefficient; Φ_B is the barrier height, which is either the hot electron energy differences with the LUMO of the absorbate or with the CBM of the semiconductor; n is a material-dependent parameter, which is equal to 2 in metals while normally >2 in semiconductors. Here, Φ_B plays a paramount role in determining the hot carrier transfer efficiency and carrier rectification for the indirect transfer route [6,81,82]. As another important parameter, the lifetime of charge separation assesses the decay of free-carrier absorption. A longer-lived charge separation enables a higher lightenergy conversion efficiency and quantum efficiency [92]. A variety of hetero-systems containing semiconductor plasmonic nanostructures have been employed to exploit efficient architectures for hot carrier harvesting and conversion [81,83,88,89,92–94]. Sakamoto et al. reported a 33 % hot-electron injection efficiency and ~200 µs long-lived charge separation in the heterostructure of ITO nanocrystals and the SnO₂ film. Such a good performance comes from a synergy of the careful design of the Schottky barrier at ITO/transparent-oxides interfaces and selective LSPR excitation [92]. Lian *et al.* observed an exceptionally long-lived charge separation of >273 µs in a plasmonic p-n junction of CdS/Cu₇S₄, profiting from the internal electric potential (the depletion region) for ultrafast hot-carrier separation [93].

The study of quantum pathways for indirect hot-carrier transfer are another research frontier, commonly studied by transient absorption (TA) and time-resolved infrared (TR-IR) spectroscopies. Shan et al. described the hot-carrier dynamics in a van der Waals heterostructure of MoS₂ and graphene quantum dots by employing the biphasic electron injection model and modified rate equations. It reveals four main processes governing the carrier migration: hot-electron injection, hot-electron cooling, cold-electron injection, and back electron transfer. Furthermore, the quantum confinement effect of graphene quantum dots drastically affects interfacial dynamics, where their sizes dictate the rates of cold electron injection and back electron transfer [88]. Zhou *et al.* inspect the hot-carrier kinetics in F- and In- doped CdO (FICO) nanocrystals. Within 50 fs after Landau damping, the hot electrons transfer to neighboring Rhodamine B (RhB) molecules with an efficiency of 1.4 %. The ultrafast transfer rate effectively prohibits the energy loss and thermal

relaxation stemming from electron-electron and electron-phonon scattering [81].

The direct transfer route has sparked scientific interest due to the absence of intermediate carrier transfer prohibiting interface electron–electron scattering. The direct transfer accomplishes via chemical interface damping (CID). Specifically, CID launches hybridized surface states at the nanocrystal-absorbate interface under different interface environments [69,82]. Thus, the CID-driven direct transfer supplies additional plasmon decay channels allowing higher transfer efficiency and lower energy losses. There are typically two mechanisms for the direct transfer of hot carriers, as sketched in Fig. 3, taking the heterostructure of plasmonic semiconductors in contact with another semiconductor as an example. The first route, the direct interfacial charge transfer transition (DICTT), launches hot carriers directly in the nearby semiconductor/absorbate, leaving carriers of the opposite charge in the plasmonic semiconductor [78]. The other process, the plasmon-induced interfacial charge transfer transition (PICTT), proceeds under the assistance of pre-excited plasmons. The PICTT exerts an overwhelming advantage in hot carrier transfer efficiency, attributed to hot-carrier trapping and long-lived charge separation [83]. For instance, CdS/CuS heterogeneous nanocrystals reach an ultrahigh quantum yield of 19 % for hot carrier transfer via PICTT [95].

Due to their energetic nature, hot carriers effectively accelerate redox reactions and promote device performance around plasmonic platforms. Plasmon-induced chemical conversions, such as dimerization, have been implemented on $Cu_{2-x}Se$ nanocrystal surfaces [94]. In addition, hot carrier transfer also sees high potential in prompting chemical and physical evolutions, including plasmon-induced desorption, magnetic phase transition, phase transition in VO₂, and electrical doping of 2D materials [96–98]. It also paves the way for plasmon-mediated photocatalysis, electrocatalysis, photovoltaics, photodetection, nano-metal working, and photothermal therapy [7–10,27,73,82,90,99].

2.2.3. Thermal dissipation induced by hot-carrier damping

Local plasmonic thermalization initiates from the relaxation of hot carriers, which dissipates heat towards the crystal lattice and environmental surroundings [8]. The thermal dissipation to the lattice is caused by electron–phonon collisions within 10 ps of delay time from the hot carrier generation, as shown in Fig. 3. The direct impacts are lattice expansion and phonon generation. A radial molecular vibrational mode — the "breathing mode" — forms during this phase, as expressed as:

$$T_{br}^{(n)} = (2\pi R) / (\chi_n c_l),$$
 (16)

where T_{br} is the oscillation period of the "breathing mode", R is the radius of the nanoparticles, and c_l is the longitudinal speed of sound. χ_n is the eigenvalue in $\chi_n \cot \chi_n = 1 - (\chi_n c_l)/(2c_l)^2$, in which c_l is the transverse speed of sound [100]. Equation (16) establishes when assuming electron-lattice collisions happen homogeneously and isotropically in spherical nanoparticles. It yields a T_{br} duration on the ps timescale.

Subsequently, hot carriers radiate heat toward the immediate environment, driven mainly by phonon–phonon interactions. This process typically lasts from 10 ps to 10 ns, and the temperature gradient is given by:

$$\rho(\mathbf{r})c(\mathbf{r})\frac{\partial T(\mathbf{r},t)}{\partial t} = K\Delta T(\mathbf{r},t) + S(\mathbf{r},t),$$
(17)

where $\rho(\mathbf{r})$ is the mass density, $c(\mathbf{r})$ is the specific heat, $T(\mathbf{r},t)$ is the temperature at time *t* and position \mathbf{r} outside a plasmonic nanoparticle. *K* is the thermal conductivity, and $S(\mathbf{r}, t)$ is related to the thermal generation in the nanoparticle induced by laser radiation [101]. When subject to continuous wave illumination, Equation (11) can be simplified as:

$$\Delta T(\mathbf{r}) = \frac{V_{NP}S(\mathbf{r},t)}{4\pi K r},\tag{18}$$

where $\Delta T(\mathbf{r})$ is the temperature difference between a single spherical nanoparticle and the ambient, and V_{NP} is the nanoparticle volume [102]. Eventually, the system establishes thermal equilibrium when reaching the Fermi-Dirac distribution [10,78,81,82].

Compared to global heating, the plasmon-induced local thermal field supports higher controllability, heating rate, and energy efficiency. Therefore, plasmonic thermalization benefits surface modification, phase transition, nanocrystal growth, and chemical separation [8,91]. The plasmon-induced heat can also convert into other forms of energy inside the contacted adsorbates. This effect has been leveraged for thermal therapy [11,12,103–106], photodetection [9,107], catalysis [108–110], seawater desalination [111], steam generation [112] and solar energy harvesting [10].

2.3. Characterization of surface plasmons

2.3.1. Optical characterization

Spectroscopic techniques, particularly absorption spectroscopy, Fourier-transform infrared spectroscopy (FTIR), TA spectroscopy and TR-IR spectroscopy, are most widely employed for plasmon detection. They probe the incident signals' absorption, transmission, or reflection while monitoring peak shifts. Hence, spectroscopic techniques allow straightforward, fast, and nondestructive detection in specimens of different structural natures [113]. FTIR fits better for examining semiconductor plasmons, whose intrinsic frequencies are mainly in the infrared region [46,48,72,114–116]. TA spectroscopy provides reliable means to inspect the hot electron dynamics after plasmon excitation, which will be discussed in detail in the Section 2.2.3. Near-field imaging approaches often combine with optical spectroscopy, offering spatial mapping of surface plasmons at a sub-diffraction-limited resolution. The most widely used tools are scanning near-field optical microscopy (SNOM) and photoemission electron microscopy (PEEM). By focusing laser light onto the

apex of a nanoscale tip, SNOM scatters the near-field plasmonic signals into detectable far-field propagating optical waves [1]. Therefore, it allows to extract the amplitude, phase and complex dielectric constant of the measured plasmonic nanomaterials. To date, SNOM has reached the spatial resolution down to the sub-10 nm scale, depending on the radius of the tip curvature. As an example, Fig. 4a presents a SNOM mapping of a plasmonic VO₂ nanostripe [1,117]. Kelvin probe force microscopy (KPFM) is an alternative tip-scanning tool. It images the surface potential of a plasmonic structure by mapping the near-field enhancement or work function differences induced by excited surface plasmons [78]. In contrast to SNOM, PEEM collects emitted electrons, providing high-resolution spatial sampling and fs-timescale plasmon dynamics [56]. Photon-induced near-field electron microscopy (PINEM) is similar but excites plasmons by a UV pulse with an adjustable delay [14,16].

2.3.2. Electron-activated plasmon detection

Electron-activated plasmon detection relies on a high-energy electron beam to excite plasmons. Among all techniques, electron energy-loss spectroscopy (EELS) is a versatile and powerful tool with Ångstrom resolution, incorporated into a transmission electron microscopy (TEM) or a scanning transmission electron microscopy. In EELS, the inelastic scattering between the specimen and transmitted electron beam causes its energy losses and inner-shell ionizations, as characteristic of the atomic composition. When detecting a plasmonic nanostructure, the high-energy transmitted electron beam functions as an electromagnetic source to launch plasmons, which can be visualized by EELS. Hence, EELS provides diverse information about plasmons, covering their energy, distribution, density, and mode orders. Fig. 4d showcases the low-loss EELS spectra and fitted intensity maps of monoclinic MoO_2 nanoribbons [118]. In the nanoribbons, electrons oscillate along the lateral direction, which leads to longitudinal multipolar plasmonic modes at energies of 0.14, 0.24, and 0.35 eV. The EELS-fitted intensity maps in Fig. 4e manifest homogenous spatial distribution across the entire nanoribbon at higher excited energies of 1.82 and 3.32 eV. They are attributed separately to a transversal SPP mode and interband transitions in the MoO_2 electronic structure. Despite the extremely high resolution and versatility, EELS possesses the primary downside of ultrathin specimen requirement (typically <100 nm).

Cathodoluminescence (CL) nanoscopy serves as a complementary to EELS, where the photon emission happens under the electron beam in a scanning electron microscope. Hence, CL allows the characterization of thicker samples [16]. A CL nanoscope images the projected radiative LDOSs in a plasmonic structure along the electron trajectory. Zu *et al.* utilized CL nanoscopy to inspect the distribution and intensity of chiral radiative LDOSs in a heterostructure of WSe₂ nanodisks and Au nanoantennas [66]. SPP detection in an integrated circuit has recently been developed, which usually resorts to an avalanche photodiode with ultrahigh sensitivity [79]. This on-chip strategy with all-near-field coupling enables extremely high plasmon detection efficiency and imaging resolution. Moreover, deep learning techniques have been harnessed for plasmon characterization and metasurface design, where a deep neural network retrieves the near-field plasmon interaction from far-field measurements [119].

2.3.3. Hot carrier detection

TA spectroscopy is a pump–probe technique to study ultrafast hot-carrier dynamics with fs-scale time resolution [87,88]. It relies on a strong pump beam and a weaker probe beam from an ultrashort laser pulse. The pump pulse excites the sample, while the probe arrives at the sample with a delay time of $\Delta \tau$. On the detection side, a photomultiplier records the differences in reflected optical signals as a function of $\Delta \tau$ between the arrival of pump and probe pulses. TA spectra of plasmonic FICO nanocrystals in Fig. 5a present the hot carrier kinetics during Landau damping and thermalization [81]. The 400–700 nm probe light has a 0.05 ps delay from the 1650-nm pump laser, where the probe is generated by focusing the 1650-nm pulse onto a BBO crystal. At 450-nm probing, the induced absorption ($\Delta T/T$, where *T* is the optical transmittance) starts immediately after pumping, as manifested by the left image in Fig. 5a. By contrast, the onset of the induced absorption at 670 nm initiates at 0.35 ps after pumping, as revealed by the right image in Fig. 5a.



Fig. 5. Hot carrier characterization and external susceptibility of plasmonic semiconductors. (a) Transient absorption (TA) spectra of F- and In- codoped CdO (FICO) nanocrystals at different delay times (-0.05 to 0.3 ps) under the radiation of 400–490 nm (left) and 500–700 nm (right). Reproduced with permission [81]. Copyright 2020, Springer Nature. (b) Schematic of carrier distribution of different induced absorption (IA) processes after hot carrier generation (left) and thermalization (right) through the electron–electron (e-e) and electron–phonon (e-ph) processes. Reproduced with permission [81]. Copyright 2020, Springer Nature.

sketched in Fig. 5b, the pump–probe measurements at 450 nm and 670 nm represent the Landau damping and hot-carrier thermalization, respectively. According to Fermi-Dirac distribution and parabolic band dispersion, the electron temperature reaches 4500 K at 0.35 ps with a thermalization lifetime of 150 fs. Eventually, the induced absorption decay to 0 at 1.35 ps, reaching the equilibrium of energy relaxation. Therefore, TA spectra offer a wealth of kinetic information of hot carriers, including the decay lifetime, carrier temperature, thermalization rate and transfer rate. Recently, technological advances underpin the real-space visualization of hot carriers by resorting to scanning tunneling microscopy (STM) and scanning noise microscopy (SNoiM) [78]. The visualization is implemented by transferring hot carriers to target molecules and then detecting the local environmental fluctuations, which refers to the surface charge propagation in STM and local current fluctuation in SNoiM, respectively.

3. Representative plasmonic semiconductors

3.1. Classical semiconductor compounds

3.1.1. Conductive metal oxides (CMOs)

CMOs are sophisticated plasmonic platforms featuring high transparency in the visible spectrum. Their robust plasmonic response originates from extrinsic and intrinsic doping [33]. Externally induced dopants dominantly contribute to free carriers in extrinsically doped CMOs, which retain a full stoichiometry of the original compound. The prevailing stoichiometric plasmonic CMOs include indium oxide (In_2O_3), zinc oxide (ZnO), tin oxide (SnO_2), cerium oxide (CeO_2), and iron oxide (Fe_2O_3) [4,28,29]. Conversely, free carriers can also be induced by deficiencies such as vacancies in crystal lattices, resulting in intrinsic doping or self-doping. Consequently, the stoichiometry in such plasmonic semiconductors deviates from the theoretical value and are therefore known as the non-stoichiometric semiconductors. The main nonstoichiometric plasmonic semiconductors are cadmium oxide (CdO_3), tianium dioxide (TiO_2), bismuth oxide (Bi_2O_{3-x}) [7], cuprous oxide ($Cu_{2-x}O$) [120], ruthenium oxide (RuO_2) [121], zirconium oxide (ZrO_2), osmium dioxide (OsO_2) [28] and rhenium trioxide (ReO_3) [122].



Fig. 6. Crystallographic structures of representative plasmonic semiconductors.

3.1.1.1. In_2O_3 . Intrinsic In_2O_3 is an *n*-type semiconductor with a bandgap of ~2.9 eV. In 5 s and O 2p orbitals occupy its CBM and valence band maximum (VBM), respectively. Intrinsic In_2O_3 possesses a cubic crystal, as depicted in Fig. 6. It tolerates a multitude of external dopants, including but not limited to Sn, Ti, Sb, Mo, Ce, Fe, Cr, and F [123]. Hence, In_2O_3 features a diversity of plasmonic characters and application scenarios. Besides, the extent of state hybridization critically affects optical losses in plasmonic In_2O_3 , where the plasmonic Q-factor and carrier mobility are synergistically enhanced when the impurity scattering is spatially separated from the conduction channel, for example, in Mo- and Ce- doped In_2O_3 (Mo: In_2O_3 and Ce: In_2O_3) [23,124,125]. The anion dopants, typically F, could provide shallow donors with rearrangeable dopant distribution and suppressed impurity scattering; therefore, they contribute to the cooperative enhancement of the near-field and carrier mobility [3,46,72,126,127]. ITO is a prevailing plasmon-host semiconductor material that has been widely studied and used. ITO allows tuning of the plasmonic response over a broad NIR to MIR range with multifunctionality. It also gives access to near-zero $\varepsilon_1(\omega)$ to sustain the epsilon-near-zero (ENZ) performance, providing large-scale modulation of plasmonic behaviour for integrated modulators [24,128]. The ENZ phenomenon will be further explained in detail in Sections 3.1.4 and 5.1.4. The ITO extinction spectrum features a spectral asymmetry due to its low ε_{∞} [29]. In Fe-doped ITO (Fe:ITO), Sn dopants simultaneously serve as free-carrier donors and interacting mediators for distant Fe³⁺ ions, supporting the multifunctionality of plasmonics and magnetization [129,130].

3.1.1.2. *ZnO*. Intrinsic ZnO is an *n*-type semiconductor with a wide bandgap of 3.37 eV and a large exciton binding energy of 60 meV [131–134]. As sketched in Fig. 6, Zn atom sites in the ZnO wurtzite structure are typically replaced by cation dopants to excite plasmons, such as Al, In, Ga, Mg, or Ge [135–139]. In addition to source abundance and non-toxicity, doped ZnO possesses the key assets of broad spectral range and high tunability of plasmonic properties. Via a non-injection synthetic protocol, doped ZnO supports ultrahigh doping levels with a dopant-to-Zn ratio of over 15 % without introducing impurity phases [136–139]. Hence, the central plasmon frequency in Al-doped ZnO (Al:ZnO) nanocrystals covers a spectral range of ~5000 nm (1000–3200 cm⁻¹) [135,140,141]. Post-synthetic approaches such as photodoping or redox reactions support plasmon engineering over a broader range and greater extent in a reversible manner [28,142,143]. Plasmonic ZnO has become a promising alternative to ITO in energy harvesting, photocatalysis, photon detection, and solar cells [2,140,141,144].

3.1.1.3. *CdO*. Plasmonic, non-stoichiometric CdO is compelling due to its intrinsic near-metallic conductivity, reaching the highest mobility and the best IR plasmonic response among CMOs. These superior properties originate from the high density of oxygen vacancies and cadmium interstitials in its rock salt structure (Fig. 6) [145,146]. Nevertheless, the practical uses of CdO are constrained by its toxicity. CdO features a symmetric NIR plasmonic band with a small *FWHM*, ascribed to the high carrier mobility and background dielectric constant (ε_{∞}) [128,147]. Via extrinsic doping with In, Dy, Ga, Al, Sn, or F, CdO converts its intrinsic indirect bandgap of 0.84 eV to a significantly widened bandgap of 2.2–3.1 eV [28,148]. The most prominent candidate is In-doped CdO (ICO, Fig. 6) of highly reliable and manipulatable plasmonic nature, reaching a high Q-factor up to 8.2, the extinction coefficient of 10^8 – 10^9 M⁻¹cm⁻¹, and σ_{ext} comparable to that of metals [4,23,41]. By additional F doping, FICO enables an electron density of up to 10^{21} cm⁻³, tuneable plasma frequencies in the 1500–3300 nm range, and Q-factors up to 12.2 [23,128,147,149,150].

3.1.1.4. TiO₂. As an *n*-type semiconductor with an indirect bandgap of 3.2 eV, TiO₂ exhibits a variety of crystalline structures. Plasmonic TiO_{2-x} commonly possesses the anatase structure (Fig. 6) with massive oxygen vacancies and compensating Ti³⁺ ions, reaching a maximal carrier density in the magnitude of 10^{21} cm⁻³ [151,152]. Excess oxygen deficiencies cause bandgap narrowing in TiO_{2-x} owhere the interband transition governs the plasmon resonance [151]. Under the synergy of near-field light confinement and plasmon hybridization, the LSP frequency in TiO_{2-x} covers an ultrabroad 300–5000 nm spectral domain, even exceeding the entire solar energy spectrum [10,153]. Uniquely, self-assembled TiO_{2-x} nanocrystals present an anisotropic plasmonic response. The anisotropy stems from the effective-mass deviation along different axes in the anatase structure [151]. In addition, extrinsic doping by Nb, N or F (forming Nb:TiO₂, TiN_{1-x}O_x F:TiO₂ respectively) and *ex-situ* electrochemical biasing could further reinforce the active and anisotropic tailoring of plasmons in TiO_{2-x} [151,153–155]. Studies of plasmonic TiO_{2-x} are relatively scarce compared to other CMOs since the intensity of its plasmon resonances remains inferior.

3.1.2. Metal chalcogenides

Group IB chalcogenides are prevalent *p*-type plasmonic semiconductors. Being the primary category, copper chalcogenides $Cu_{2-x}E$, $(E = S, Se, or Te; x = 0 \sim 1)$ could tolerate a higher free-carrier density up to the magnitude of 10^{23} cm⁻³ and support a more pronounced NIR extinction [156]. In addition, they also feature high thermal conductivity, low fabrication cost, and low cytotoxicity. Therefore, they have become intriguing candidates in photovoltaics, bioimaging, biosensing, and phototherapy [11,12,105,157]. As governed by the stoichiometric fluctuation, $Cu_{2-x}E$ presents large deviations in the crystal structure, bandgap, and crystal shapes. This character imparts an expanded IR plasmonic response towards lower wavelengths of copper chalcogenides. Under high doping levels, $Cu_{2-x}E$ suffers from poor structural controllability and non-avoidable by-products. Moreover, $Cu_{2-x}E$ faces the instability issue where the plasmon resonance quenches under thermal treatment and light stimuli [158].

Fig. 6 depicts the most popular cubic structure of $Cu_{2,x}E$, in which chalcogenide atoms constitute the cubic frame, and Cu atoms occupy interstitial sites in the lattice. $Cu_{2,x}E$ also presents a variety of other crystalline structures, herein taking $Cu_{2,x}S$ (bandgaps of 1.2–2.6 eV), for example. Observed $Cu_{2,x}S$ structures encompass chalcocite (Cu_2S), djurleite ($Cu_{1.94}S$), digenite ($Cu_{1.8}S$), roxbyite ($Cu_{1.75}S$), anilite ($Cu_{1.4}S$), spionkopite ($Cu_{1.39}S$) and covellite (Cu_2). (Laptic compass chalcocite in these systems donate substantial free holes governing the plasmon characters. The plasmons in $Cu_{2,x}E$, typically oscillating in the NIR region, are highly tailorable via

defect engineering. Again, we take $Cu_{2-x}S$ as an example. One rational route is to harness the redox reaction for ion insertion or extraction in the $Cu_{2-x}S$ lattice, which alters the concentration of Cu vacancies. During the continuous-flow synthesis of $Cu_{2-x}S$ quantum dots (QDs), the plasmon frequency shifts by 529 nm via changing the reagent injection rate. Similar phenomena were observed in ternary alloys $Cu_{2-x}Se_yS_{1-y}$ and $Cu_{2-x}Te_yS_{1-y}$ [33,156]. Another popular strategy is to engineer the $Cu_{2-x}S$ crystal structure to release massive Cu vacancies without changing the nanocrystal size or shape [33]. Self-doped Ag₂Se is an intriguing alternative to $Cu_{2-x}E$. Ag₂Se colloidal QDs represent ideal quantum-to-colloidal hybrids with different emission performances in response to structural changes [159]. These nanostructures support a tuneable intensity and small *FWHM* (23.7 meV) in the emission spectra thanks to the synergy of LSPRs, suppressed electron–electron scattering, and near-field energy transfer.

3.1.3. Refractory nitrides

Refractory nitrides have been a series of extraordinary plasmonic materials due to the distinctive plasmonic response down to the visible-light region, high-temperature tolerance (>1200 °C), superior chemical inertness, CMOS compatibility, and biocompatibility [9,115,160,161]. Besides, they are highly efficient in NIR plasmonic thermalization even surpassing Au. However, the refractory character produces obstacles for the material preparation of plasmonic nitrides, whereas their rich surface defects remain poorly tailorable but crucial for plasmonic behavior [161,162]. These nitrides encompass Ti_xN , Zr_xN , Nb_xN , In_xN , Ga_xN , Cr_xN , Ta_xN , and V_xN , as well as their mutual alloys and solid solutions, including $Ti_{1-x}Mg_xN$, $Ti_{1-x}Al_xN$, $Ti_{1-x}Ta_xN$, $Ti_{1-x}Ta_xN$, $Zr_{1-x}Ta_xN$

3.1.4. III-V semiconductors

Plasmonic III–V semiconductors are particularly appealing for on-chip applications owing to their mature fabrication technologies compatible with the mainstream CMOS foundry processes. The plasmonic applications can be attained by replacing the III–V semiconductors in existing devices with degenerately doped components. Therefore, plasmonic III–V semiconductors have established themselves as building blocks for active devices in plasmonic integrated circuits of low cost, small footprint, and mass production. Despite intensive exploration, plasmonic III–V semiconductors are still inferior regarding relatively lower plasmon frequencies and conductivity [24].

So far, III–V semiconductors including ScN [68], InAs [168,169], InGaAs [170], GaN [171], GaAs [171], and InAsSb [50] have been exploited for NIR plasmonic uses. Their amphoteric nature dictates the dopants' donor/acceptor behavior, playing indispensable roles in the plasmonic response [24]. The lattice deformation is another critical factor, stemming from the atomic radii difference or electronic-induced deformations. This structural distortion alters the band structure, bond lengths, and local strain, giving the potential to reach exceedingly strong plasmon resonance. Besides, III–V semiconductors are ideal platforms for attaining ENZ behavior. The ENZ phenomenon has been observed in systems containing plasmon-polaritons, phonon-polaritons, or exciton-polaritons. A tuneable longitudinal ENZ mode is favorable for practical uses [24]. Hence, systems sustaining phonon polaritons are not the best option due to the lack of tuneability. ENZ is not accessible in metals due to high losses induced by interband transitions. Alternatively, III–V semiconductors possess polar crystalline structures and high flexibility of plasmon frequencies, while prohibiting extra-large losses induced by poor crystallinity. For instance, the polar ScN is a promising candidate. Maurya *et al.* observe the thin ScN film sustaining plasmon and phonon polaritons in the short-wavelength infrared (SWIR) and long-wavelength infrared (LWIR) ranges, respectively [68]. The ENZ effect allows an efficient light modulation and light funneling into extremely narrow (subwavelength) apertures or channels.

3.2. 2D materials

2D materials offer unique frameworks for plasmon-polaritons owing to their crystal structures with vdW stacking of covalently bonded in-plane atomic layers. As a result, they support rather large optical densities of states, high exciton binding energies, diverse quantum-confined resonant conditions, and extreme surface-to-volume ratio [58,172-175]. 2D materials allow exceedingly high-level doping via extraordinary routes including ion intercalation, electrostatic doping, and the supercritical CO₂ method [18,176]. Their distinctive structure also breeds unique plasmonic phenomena such as hyperbolic plasmons, anisotropic plasmonic response, plasmonic spintronics, and valleytronics, amongst others. Hence, emerging 2D semiconductors open a new horizon for plasmonics, although only limited materials have been explored. There are still many bottlenecks for plasmonics in 2D materials, including weak plasmon signals, the plasmon detection difficulty, and insufficient device efficiency. Besides, the physical essence of their exotic plasmonic response remains elusive. In particular, the seldom-demonstrated plasmonic vdW heterostructures hold high promise in unprecedented interface plasmonic phenomena [177].

The dispersion relation of plasmons in 2D materials is different from those in bulk materials. It is described by [48]:

)

$$\omega_p = \left(\frac{e^2}{2\varepsilon_0\varepsilon_d} n_{eff} \middle/ m^*\right)^{\frac{1}{2}} \sqrt{k_{eff}},\tag{19}$$

where n_{eff} and k_{eff} are the effective carrier density and effective wave vector, respectively. Equation (19) explains the anisotropic plasmon frequencies along different crystalline axes, which is mainly ascribed to anisotropic effective masses. The plasmon performance in 2D semiconductors is intrinsically different from that in gapless 2D semimetals like graphene. For instance, the longwavelength plasmons in massive Dirac systems (2D semiconductors) have a density dependence of $\omega_p \propto n^{1/2}$, whereas massless 2D Dirac systems (such as graphene) follow $\omega_p \propto n^{1/4}$. The damping of plasmon resonance in 2D semiconductors is derived from intraband transitions, while it arises from an interband transition in gapless graphene [48,177].

3.2.1. Elementary 2D materials

Plasmonics has been investigated in elementary 2D materials such as graphene, phosphorene, silicene, and germanene. Among them, graphene is the most pervasive. It possesses a layered honeycomb crystalline structure, as shown in Fig. 6 [178]. Graphene features a band structure with Dirac cones, giving rise to metallic mobility, ultralow resistivities of $10^{-6} \Omega$ cm, ultrahigh thermal conductivity (~4000 $W \cdot m^{-1} \cdot K^{-1}$), and excellent mechanical flexibility [179–182]. The gapless nature of graphene nevertheless hinders its applications in nanoelectronics. The breaking of inversion symmetry is essential for bandgap opening in graphene. Conventionally, it is accomplished via gating, altering substrates, applying magnetic fields, or breaking it into nm-scale lateral dimensions.

Graphene serves as an excellent plasmonic medium in the MIR-THz range [183]. Graphene plasmons feature strong light confinement and high plasmon flexibility tailored by the electrostatic field, high-frequency pulses, and dielectric surroundings [184]. Chen et al. leveraged SNOM to achieve real-space visualization of plasmon fields in graphene for the first time [185]. Under IR light radiation, a graphene ribbon sustains two distinct modes, rendering itself as a plasmonic cavity with tuneable, switchable resonant frequencies and exceedingly small mode volume. In recent years, twisted bilayer graphene (TBG) has been an emerging frontier for graphene plasmonics, forming by overlaying two graphene layers with a twist angle. The atomic reconstruction and interlayer coupling produce exotic plasmon modes in TBG. Sunku et al. detected propagating plasmons on TBG via IR nano-imaging [184]. As shown in Fig. 7a, the Drude-like plasmons convert the TBG into natural plasmon photonic crystals, providing a controllable pathway for nanoscale light control. Brev et al. observed chiral edge plasmons in a biased TBG [186]. Different from Drude-like polaritons, the



Fig. 7. Representative plasmonic 2D materials. (a) IR nano-imaging of photonic crystal formed by Drude-like plasmons in twisted bilayer graphene. Inset: dark-field TEM image of the TBG. Reproduced with permission [184]. Copyright 2018, American Association for the Advancement of Science. (b) Schematic of electron transition in $W_{18}O_{49}$ under light radiation, where $W^{5+}W^{5+}$ pairs act as local electron reservoirs for LSPRs. Reproduced with permission [87]. Copyright 2022, Wiley-VCH. (c) Left: optical microscope image of a mechanically exfoliated WTe₂ thin film; Sketch of a WTe₂ skew ribbon array for hyperbolic plasmon detection. Right: isofrequency contours in the wavevector space (qa-qb) under different frequencies (250–500 cm⁻¹), which reveal the existence of hyperbolic and elliptic plasmons. Reproduced with permission [48]. Copyright 2020, Springer Nature. (d) Left: atomic model of MoS₂ nanoflakes where the tunable localized resonance originates from S vacancies; right: scanning transmission electron microscopy (STEM) image of MoS₂ verifying the atomic model. Reproduced with permission [110]. Copyright 2018, Royal Society of Chemistry.

chiral edge plasmons result from the collective intra-edge excitation at the AB-BA interfaces. The breaking of rotational symmetry opens a tuneable bandgap around the Dirac cone. Plasmonics in graphene has seen great potential in THz photodetection, hot-carrier-assisted energy harvesting, thermal management, spectroscopic sensing, and large-area fast imaging [18,86,96,107,181,187–191].

Black phosphorus (with its monolayer form phosphorene) has a puckered honeycomb crystalline structure and tuneable bandgap of \sim 0.3–2 eV [192–194]. Stemming from the anisotropic band structure and effective mass, black phosphorus retains different in-phase and out-of-phase oscillating motions of free holes [195]. Hence, plasmons in black phosphorus disperse differently along the armchair and zigzag directions, which support higher resonance frequency along the armchair direction due to smaller effective mass [177]. Black phosphorus also underpins a high potential in ultrafast switchable nano-optics. In a SiO₂/black phosphorus/SiO₂ heterostructure, Huber *et al.* detected the fs photo-switching behavior in black phosphorous [70]. The surface plasmon mode on black phosphorus couples with the surface phonon mode on SiO₂, generating hybrid interface polaritons. The coherent interaction resulted in an excellent switching performance activated by the interband excitation in ~50 fs and presented high contrast across the mode lifetime of <5 ps. Plasmons in black phosphorous are tailorable by potassium doping, which results in an external strain and out-of-plane electric field. Silicene and germanene are emerging 2D semiconductors with buckled honeycomb structures. When applying a vertical electric field, these materials undergo a phase transition and alteration of plasmon dispersion. Under this circumstance, silicene and germanene evolve from insulators to metals or topological insulators [177].

3.2.2. Transition metal oxides (TMOs)

2D TMOs, representatively molybdenum trioxide (MO_{3-x}) and tungsten oxide (WO_{3-x}) have been the most widely investigated 2D materials. They exhibit the best performance among semiconductor plasmonic materials in fields such as SERS, photocatalysis, and bio-applications [87,118,176,196,197]. These compounds enjoy the favorable attributes of metallic conductivity, high melting points, excellent chemical and thermal stability, and low cost [6]. Despite the insufficient free-carrier concentration in self-doped 2D TMOs, they offer unconventional carrier injection strategies such as proton doping, ligand exchange, and surface coordination design. These exceptional approaches offer the 2D TMOs viable means to reach a high free-carrier density and a long-lived plasmonic field over an ultrabroad UV–MIR spectral range [29,103]. 2D plasmonic TMOs also support lower losses, attributed to the large effective mass and high carrier mobility [191]. The primary challenges for these materials lie in the relatively poor controllability over their morphology, dimension, and surface behavior.

3.2.2.1. $MoO_{3.x}$. Intrinsic MoO₃ is an *n*-type semiconductor with a direct bandgap of 3.2 eV. It possesses two crystalline structures: the orthorhombic α-phase and the monoclinic β-phase [198,199]. 2D α-MoO₃ is ambiently stable, whose crystalline structure is depicted in Fig. 6, with MoO₆ octahedra corner-sharing along the *a*-axis and edge-sharing along the *c*-axis in each planar unit of double atomic layers [200]. Ion intercalation and Mo partial reduction give the high flexibility of oxygen deficiencies and plasmon characters in α-MoO_{3-x} [198]. On the other hand, the naturally metastable β-MoO_{3-x} exhibits a rutile structure. Zhu *et al.* observed plasmonic response in monolithic MoO₂ nanostructures, which has a distorted rutile β-MoO_{3-x} structure with two distinct sets of Mo-Mo bond lengths: 2.578 and 3.063 Å [118]. These MoO₂ nanoribbons support longitudinal and transverse plasmon modes, where a highly pronounced resonant interaction is attributed to the Mo *d* orbitals. Plasmon tailoring in MoO_{3-x} is accessible via extrinsic doping, especially Co or Ni doping [176,196,201–204]. Recently, an electron–proton co-doping protocol are developed to form metal-like H_xMoO₃ [118]. This emerging plasmonic phase offers a free-carrier concentration of 10^{21} cm⁻³, a long-lived plasmonic mode, and a record-high detection limit of 10^{-9} mol/L in SERS. Twistronics also demonstrates the potential for control of plasmon dispersion. Phonon polaritons in twisted α-MoO₃ bilayers have revealed a hyperbolic-to-elliptical topological transition [205].

3.2.2.2. WO_{3-x} Intrinsic WO₃ is an *n*-type semiconductor with a bandgap energy of 2.6 eV and a monoclinic crystalline structure, as illustrated in Fig. 6. Anoxic WO_{3-x} does not drastically distort the original lattice. Instead, it forms a partially incomplete perovskite-type ABO₃ lattice, as sketched in Fig. 6 [204,206]. This structure creates tunnels within the basic octahedron, giving rise to a rich suite of stoichiometries in WO_{3-x} (x = 0.1–1.03) [108,115,207]. Lu *et al.* found that the periodically arranged W⁵⁺-W⁵⁺ pairs in W₁₈O₄₉ serve as reservoirs for localized free electrons, as shown in Fig. 7b, bringing in intrinsic LSPRs [87]. Few-layer WO_{3-x} nanoplatelets with enormous aspect ratios reach a high electron density of 4×10^{22} cm⁻³ [207]. The metalloid WO_{3-x} enables plasma frequencies to cover the whole solar spectrum [51,115,201,208,209]. Cesium-doped tungsten oxide (Cs:WO_{3-x}) generates dual plasmonic modes, where Cs⁺ ions occupy open channels in the WO_{3-x} lattice for an evident frequency shift [51,206]. The alloy between WO_{3-x} and MOO_{3-x} highly crystallized Mo_xW_{1-x}O_{3-y}, gives a significantly amplified LSPR intensity owing to abundant vacancies in the lattice, predominantly oxygen vacancies and vacancies from mutual doping of Mo and W ions [210,211]. Various redox processes, such as solar irradiation or oxygen annealing, also allow defect engineering for LSPR manipulation [103,191].

To date, MO_{3-x} and WO_{3-x} have demonstrated excellent performance in SERS [212], selective gas sensors [204], solar-driven nitrogen fixation [213], *in vivo* bioimaging [214], catalysis [73,87], photothermal therapy [104], field emission displays [215,216], electrochromic devices [217].

3.2.3. Transition metal dichalcogenides (TMDCs)

Plasmonic TMDCs, despite the weak plasmon resonance, present unique plasmon behavior. TMDCs sustain hyperbolic plasmon polaritons, spin–orbit coupling, and surface polaritons in topological insulators [218]. Besides, TMDCs have a finite bandgap tunable as a function of thickness [28,219]. Here, we will select the representative MoS₂ and WTe₂ to interpret the extraordinary plasmonic phenomena in TMDCs. Fig. 6 shows the crystalline structures of WTe₂, illustrating an orthorhombic crystalline structure with W atom

Table 1 Properties and applications of representative plasmonic semiconductors.

Category	Material	Crystalline structure	Intrinsic bandgap	Plasmon frequency (µm)	Free carrier concentration (cm^{-3})	Origin of free carriers	Applications	Ref.
Conductive metal oxides	In ₂ O ₃	Cubic	3.7 (direct)	1.25–3.9	$\begin{array}{c} 3.24 \times 10^{19} 2.8 \\ \times \ 10^{22} \end{array}$	Extrinsic doping: Sn (ITO), Ti, Sb, Mo, Ce, Fe,	 Integrated photonics Phase modulators Fiber sensors 	[13,72,75,115,124,126,129,130,239-241]
	ZnO	Wurtzite	3.37 (direct)	1.8–5	$\substack{\textbf{4.2}\times10^{19}\text{-}\textbf{8.7}\times\\10^{21}}$	Extrinsic doping: Al, In,	- SERS	[142,143,202,242–244]
	CdO	Rocksalt	2.57 (direct)	1.5-~6	3.1×10^{19} -1.07 × 10^{21}	 Oxygen vacancies Surface Cd²⁺ Extrinsic doping: In, Dy Ga Al Sn F 	 Electrochromic smart windows ENZ-based modulators 	[128,145–147,239]
	TiO ₂	Anatase	3.2 (indirect)	2–5	$\begin{array}{c} 2.5\times10^{19} 1.12 \\ \times \ 10^{21} \end{array}$	 Oxygen vacancies and compensating Ti³⁺ ions Extrinsic doping: Nb 	 Photocatalysis SERS Plasmontronics for quantum technology Smart windows Photodetectors 	[99,154,245-247]
Metal chalcogenides	Cu _{2-x} S	Cubic	1.2-2.6 (direct)	0.8–2.24	$2.64 \times 10^{21} \rightarrow 1$ $\times 10^{23}$	- Copper vacancies	- Bio imaging	[12,115,156,207,248–250]
	Cu _{2-x} Se			1.05–1.7	6×10^{20} -1.42 × 10^{21}	- moys with 5, 5c, 1c	 Photocatalysis Field-effect transistors 	[11,105,157,250,251]
	Ag _{2-x} Se	Orthorhombic	0.2 and 1.1	5.6–7.25	$\frac{1.5\times10^{20}3.5\times10^{20$	Silver vacancies	 Solar water splitting Photo thermoelectric generators SERS 	[159]
Refractory nitride	Ti _x N (x < 1)	Rocksalt	3.4 (direct)	0.45–1.05	1×10^{22} –5.1 × 10 ²²	 Titanium vacancies Defects related to surface oxidization 	 Plasmonic waveguides Emitters Photodetectors Chemical- and biosensing Photothermal therapy Solar cells Nano heat source 	[9,55,106,160,164,165,167,252,253]
III-V semiconductors	ScN	Cubic	0.9 (indirect)	1.83–27.8	$\begin{array}{c} 5\times 10^{18} 1.6\times \\ 10^{21} \end{array}$	 Intrinsic defects External doping: Al, 	 Integrated plasmonic circuits for optical 	[68]
	InAs	Zinc Blende	0.35 (direct)	9–11	$6 imes 10^{18}$ –1.5 $ imes$ 10 20	Mg, Si, Ge, P - Donor-type surface and	communication - Plasmonic lasers	[163,168,254]
	InGaAs		0.75-1.2	8	$1\times10^{18}4\times10^{18}$	edge states	 Plasmonic waveguides 	[163,255,256]
	GaAs		1.42 (direct)	>6	$\begin{array}{c} 7.5\times10^{19} 2.44 \\ \times\10^{21} \end{array}$	U	PhotodetectorsHyperbolic or ENZ	[163,256,257]
	InAsSb		0.75–0.94	6.26–8	${\substack{1 \times 10^{19} - 3.4 \times \\ 10^{19}}}$		metamaterials - Solar-energy harvesting	[50,163]
2D materials	MoO _{3-x}	Orthorhombic and monoclinic	3.2 (direct)	0.63–0.95	$\begin{array}{c} 8.5\times10^{21}\rightarrow1\times\\ 10^{22} \end{array}$	 Oxygen vacancies Abundant delocalized 	- SERS - Bioimaging	[116,118,176,198,210,258]
	WO _{3-x}	Monoclinic and incomplete perovskite	2.6 (indirect)	0.75–1.4	$\begin{array}{c} 3.2 \times 10^{22} 8.7 \times \\ 10^{22} \end{array}$	electrons in Mo/W d orbitals - Ionic intercalation	 Photothermal therapy Photo- and electro- catalysis Electrochromic displays 	[65,108,197,210,259–264]

(continued on next page)

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Table 1 (continued)

Category	Material	Crystalline structure	Intrinsic bandgap	Plasmon frequency (µm)	Free carrier concentration (cm ⁻³)	Origin of free carriers	Applications	Ref.
	Black Phosphorus MoS ₂	Puckered honeycomb Hexagonal	0.3–2 (indirect–direct) 1.2–1.9 (indirect–direct)	MIR-THz	$>3 \times 10^{13} \mathrm{cm}^{-2}$ (2D)	 Extrinsic doping: Co and Ni, electron and proton doping Intrinsic defects Electrostatic doping Strain induced by K doping Sulfur vacancies in lattices 2H-1 T phase 	 Biosensing THz detection Photo- switching Photocatalysis Natural hyperbolic metamaterials Nonlinear plasmonics 	[42,70,177] [80,110,177,224]
Phase change materials	VO ₂	tetragonal-to-rutile	insulator to metal	0.62–1.88	5×10^{19} -4.9 × 10^{22}	transition - Metal-insulator transition - Extrinsic doping: W, Mg, Sb, F	 SERS THz modulators Thermochromic smart windows Wearable camouflage Encryption inks Hydrogen storage Biosensing Smart optical solar reflectors 	[97,117,162,231–233,238,265,266]

chains spreading along the *a*-axis [48,220]. The MoS_2 crystalline structure is depicted in Fig. 6, revealing a honeycomb lattice with alternating stacking of Mo and S atom layers [163,221].

3.2.3.1. Natural plasmonic hyperbolicity. Hyperbolic metamaterials present a hyperbolic isofrequency contour in the wave vector space. In the hyperbolic region, the permittivity parallel to a crystalline axis has an opposite sign to the perpendicular counterpart [177,222]. This unique topology allows highly directional plasmon propagation and ultra-high optical density of states, which holds high promise in planar photonics. TMDCs could generate natural hyperbolic plasmon polaritons, which originate from the in-plane anisotropic interplay of intraband and interband transitions. The natural hyperbolicity in 2D materials retains even higher electromagnetic confinement in a broader wavelength range towards THz frequencies. Besides, 2D materials allow active modulation of inplane hyperbolic plasmon propagation via chemical doping, temperature control, and electric gating. Wang *et al.* observed natural hyperbolic plasmons in WTe₂ metasurfaces, as shown by the isofrequency contour map of plasmons in Fig. 7c [48]. The WTe₂ metasurface experienced an elliptic-to-hyperbolic topological transition at 10 K across the 429–632 cm⁻¹ hyperbolic regime. At the boundary of the topological transition, plasmons dominantly propagate along the *a*-axis. The spectral weight vanishes along the *b*-axis. Other 2D platforms also demonstrate plasmonic hyperbolicity even at room temperature; for instance, graphene stacked with hexagonal boron nitride (h-BN) [177].

WTe₂ retains other novel quantum statuses, such as being a type-II Weyl semimetal topological insulator (TI). TIs show a topological character of the wave function, which supports a metallic conductivity on the surface while being insulated in the interior. The topological surface states endow the WTe₂ TI with a MIR–THz plasmon resonance in the range. Other 2D TIs, such as Bi₂Se₃, Bi₂Te₃, Sb₂Te₃, or Bi_{1.5}Sb_{0.5}Te_{1.8}Se_{1.2}, are also capable of launching plasmon modes in diverse geometry of gratings, core–shell particles, and nanoarrays [6,223].



Fig. 8. Dopant behaviour in plasmonic semiconductor nanostructures. (a) Band structures of n- and p-type semiconductors, reflecting the disturbance of the host bandgap exerted by dopants. Reproduced with permission [23]. Copyright 2018, American Chemical Society. (b) Evolution of the density of states (DOS) in H-doped MoO₃, resulting in the semiconductor-to-metallic phase transformation. Reproduced with permission [196]. Copyright 2020, Wiley-VCH. (c) Normalized reflectivity curves of the ScN film showing the ratio of p-polarized and s-polarized intensity (R_p/R_s). Left: band of plasmon polaritons with carrier density of 1.6×10^{21} cm⁻³ and 3.3×10^{20} cm⁻³. Right: confined surface-phonon polariton mode excited by p-polarized light. Reproduced with permission [68]. Copyright 2022, American Chemical Society. (d) Schematics of dopant distributions in nanocrystals, namely, interior accumulation, homogeneous distribution and surface aggregation. Reproduced with permission [241]. Copyright 2017, American Chemical Society. (e) Normalized LSPR extinction spectra influenced by the radial dopant distribution, specifically in the ITO/In₂O₃ or In₂O₃/ITO core-shell nanostructures. Reproduced with permission [241]. Copyright 2017, American Chemical Society. (g) Band structure of surface depletion imposed by Fermi-level pinning. Reproduced with permission [241]. Copyright 2018, Springer Nature. (h) Dual-mode LSPR extinction spectra in In₂O₃-core-In-shell nanostructures. Reproduced with permission [272]. Copyright 2020, American Chemical Society.

*3.2.3.2. MoS*₂. WoS₂, even at monolayer thickness, could activate plasmon resonances via (i) phase transformation to semi-metallic states, or (ii) a large amount of sulfur vacancies in its lattice, as demonstrated by the scanning transmission electron microscopy (STEM) image in Fig. 7d [110,224,225]. The spin–orbit interaction also plays a vital role in the plasmonic behavior of MoS₂, which induces spin splitting and a beating of Friedel oscillations under external fields [177]. *n*-doped monolayer MoS₂ presents plasmon-induced polaronic quasiparticles, implying a 2D electron–plasmon coupling [80]. Plasmonic MoS₂ underpins multifunctionality owing to its phase variety [110]. Specifically, the 2H-MoS₂ phase presents advantages in catalysis, in which the localized resonance regulates carrier transfer pathways, while numerous edge defects promote the efficiency of the hydrogen evolution reaction. The 1 T-MoS₂ phase is favorable for biosensing, such as SERS and thermal therapy, which reaches 46.5 % photothermal conversion efficiency [177,221].

3.3. Phase change materials (PCMs)

A PCM undergoes a phase transition via energy exchange, for instance, a metal–insulator transition (MIT) in vanadium dioxide (VO_2) or an amorphous-to-crystalline structural transition in germanium telluride (GeTe), Ge₂Sb₂Te₅, Sb₂S₃, and Sb₂Se₃ [28,226–229]. Owing to this peculiar behavior, PCMs allow reversible, switchable, and active modulation of plasmonic properties. PCM metasurfaces also enable wavefront manipulation of the launched plasmonic mode [67]. Therefore, PCMs are useful in thermochromic coatings, encryption inks, wearable camouflage devices, and programmable on-chip planar optics [162,230–232]. In this Review, we focus our discussion on the most widely studied and used VO₂, which has an MIT point close to room temperature and a distinct modification of the IR transmittance. VO₂ has rutile and monoclinic structures in the metallic and insulating phases, respectively. The rutile structure has a relatively linear atomic arrangement along the *c*-axis (Fig. 6), while the monoclinic structure constitutes zigzag chains linked by V atoms (Fig. 6) [233].

A monoclinic metallic VO_2 phase could form by scanning an AFM tip under bias across an insulating substrate [117]. This new phase induces programmable and reversible plasmon modes with arbitrary shapes. Intriguingly, the transition between these structures in VO_2 allows the evolution of both dielectric Mie and plasmonic resonances, which provides an enormous property modulation for thermochromic and sensing applications [231].

Nevertheless, a sophisticated theoretical model is still needed to interpret all unconventional experimental observations in VO₂. Goodenough proposed a crystal field theory to interpret MIT chemistry. Above the MIT temperature, the Fermi level of metallic VO₂ is mainly occupied by the d_{\parallel} and antibonding π^* orbitals. The d_{\parallel} orbital is a split *d* orbital oriented along the *c*-axis, formed by removing the *d* band degeneracy in the octahedral VO₂ crystalline structure. During cooldown, the bandgap opening leads to an insulating phase, mostly attributed to (i) the d_{\parallel} band splitting caused by V⁴⁺ dimerization; (ii) the lifting of the energy level of π^* states. Based on this model, the VO₂ MIT has been explained by the structure-dictated Peierls transition and Mott transition governed by the electron correlation [233].

There are several approaches to trigger MIT in VO₂. The classical way is to tune the system temperature across the MIT temperature. The theoretical MIT temperature is 68 °C, but the temperature window has been broadened to 40-100 °C via atomic defect engineering [230,232,234,235]. The MIT window is also adjustable by optical (THz) and electric fields [236,237]. During the MIT in VO₂, its plasmon resonance can be activated and amplified by the intermediate products containing metallic structural fractions [236]. Upon gradual heating, VO₂ undergoes three statuses, namely, dielectric resonance, damped scattering, and plasmon resonance [231,238]. The plasmonic band spans a broad wavelength range of 620–1880 nm via the synergy of oxygen vacancies, Mg/W substitutional dopants, and surface oxidation [232].

3.4. Comparison of plasmonic semiconductors

Given the diversity of materials, we summarize the basic properties and typical application scenarios of representative plasmonic semiconductors in Table 1.

4. Plasmon tailoring in semiconductors

Highly doped semiconductors provide plasmonic platforms that allow active and versatile plasmon control. The plasmon resonance enhances and tailors the near-field intensity. Plasmon damping also plays an essential role, which induces hot-carrier exchange and local thermalization that regulate the carrier density and energy level of the whole system. As a supplement, post-synthetic approaches provide more possibility for plasmon manipulation. Plasmonic tunability has been investigated in systems including nanocrystals, metasurfaces and heterostructures.

4.1. Plasmon modulation in semiconductor nanocrystals and thin films

4.1.1. Dopant engineering

Doping is the most sophisticated strategy to modulate the plasmonic properties of semiconductors. It provides excess free carriers to generate surface plasmons, while the dopant element, density, and distribution determine the plasmon characters. Doping perturbs the band structure of host lattices, as governed by the Burstein-Moss shift and band renormalization. As shown in Fig. 8a, the Burstein-Moss shift widens the optical bandgap of a degenerate semiconductor, specifically by altering the Fermi level (E_F) via band filling [13]. The band renormalization offsets the dominating Burstein-Moss effect, where the electron–electron and electron–ion Coulomb

interactions between defects and impurities alter the electronic bandgap [13,28,81]. Dopants also cause lattice deformation, dominantly governed by the hydrostatic effect or charge-correlated deformation [24,232]. The hydrostatic effect considers the radius divergence between host and doped ions, influencing the lattice strain, band structure, doping level, carrier mobility, and scattering [124,145,244]. The charge-correlated deformation mainly causes the change in bond length with an enhanced carrier population.

4.1.1.1. Dopant types and levels. Dopants can be classified into vacancies, substitutional dopants, and interstitial dopants. In nonstoichiometric plasmonic semiconductors, vacancies are the major point defects. Taking oxygen vacancies in CMOs for example, they form shallow donor levels due to the high electron affinity of oxygen. These shallow states generate abundant active carriers and stimulate plasmon resonance [29,108,204]. Their generation is favored and more controllable in a material system with larger cation radii and a variety of oxidation states, such as WO_{3-x} [267]. In practice, oxygen vacancies are usually created by *in-situ* or *ex-situ* approaches to change the atmospheric oxygen partial pressure [251]. Substitutional dopants, which take the sites of lattice atoms, dominate in stoichiometric plasmonic semiconductors. Substitutional dopants are easily ionized, which creates shallow donor or acceptor states, depending on their relative valence compared to lattice ions. Interstitial dopants sit at interstitial sites of the lattice but hardly donate free carriers at the band edge. They are also prone to clustering, particularly in proximity to crystal defects [145]. In an extraordinary situation, the Cs_xWO_3 crystal tolerates excessive ionized Cs^+ interstitials. As shown in Fig. 6, the WO_{3-x} lattice forms numerous open tunnels, which allow large Cs^+ and additional vacancies to reside. This structure, therefore, underpins high carrier concentration and high-Q-factor plasmon resonances [206].

The co-doping strategy prompts plasmon manipulability further. So far, the fluorine cation has been the most pervasive co-dopants [72,126,129,130,149,202]. Zhu *et al.* developed a novel electron–proton co-doping route to incorporate H atoms into the MoO₃ lattice [196]. As shown by the simulated LDOS in Fig. 8b, with the progressive addition of H atoms, the semiconductor MoO₃ phase converts into metallic H_xMoO_3 (x = 0.5, 1 and 2). The electron–proton doping moves up the Fermi level (*E_F*) and induces a defect state into the original MoO₃ bandgap. As a result, the electrical conductance elevates by eight orders of magnitude in H_xMoO_3 , together with the long-lived LSPR in the ultrabroad UV–visible–NIR region. Ke *et al.* manipulated the atomic defects in Mo/W-doped VO₂ nanoparticle_s, including oxygen vacancies and W/Mo substitutional dopants [232]. The free carrier concentration is determined by competing factors



Fig. 9. Impact of crystallographic structure on the plasmonic properties of semiconductor nanocrystals. (a) LSPR absorption spectra of Ag₂Se colloidal QDs of various diameters. Reproduced with permission [159]. Copyright 2020, American Chemical Society. (b) Anisotropic plasmon dispersion in monolayer phosphorene. Reproduced with permission [177]. Copyright 2018, Royal Society of Chemistry. (c) Extinction spectra of the WTe₂ microdisk array with polarization along the a and b axes. Reproduced with permission [48]. Copyright 2020, Springer Nature. (d) MIR-range LSPR absorption spectra of TiO₂ nanocrystals with different crystal structures, as depicted on the right of (e). Reproduced with permission [76]. Copyright 2019, American Chemical Society. (e) MCD spectra of F-OLAM (blue curve) and M-OLAM (green curve) nanocrystals in the UV–visible range collected at 5 K. Reproduced with permission [76]. Copyright 2019, American Chemical Society. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

of (i) the number of valence electrons and (ii) the charge of metal cations.

In a plasmonic semiconductor, defect activation and compensation is the foremost factor dictating the doping level. During progressive dopant inclusion, the doped system consecutively undergoes the intrinsic, extrinsic and compensation doping phases. In the compensation regime, compensated defects with the opposite charge to the dopants become populated to maintain charge neutrality. Taking ITO for instance, at high interstitial Sn (Sn_{in}^{\bullet}) doping level, there exists a valence-charge imbalance between Sn_{in}^{\bullet} and the In₂O₃ matrix. To reach charge neutrality, oxygen interstitials (O_i°) with the opposite charge to Sn_{in}^{\bullet} are generated, forming defect complexes $2Sn_{in}^{\bullet} - O_i^{\circ}$. The defect compensation hampers a further increase in the carrier density. Second, the *p*- or *n*-dopant type also plays a principal role. For instance, the ScN thin film launches plasmon polaritons via oxygen doping, while phonon polaritons via magnesium doping [68]. As shown in Fig. 8c, O-doped ScN films support a tuneable SPR response in the short-wave IR, with carrier concentrations of 1.6×10^{21} cm⁻³ (the ScN (a) film) and 3.3×10^{20} cm⁻³ (the ScN (d) film). In the Mg-doped ScN film, surface-phonon polaritons couple with *p*-polarized light, leading to a dip at 626 cm⁻¹ within the *reststrahlen* band in the long-wave IR range. A third factor governing the doping level is the dopant solubility in the host matrix under thermodynamic equilibrium. Finally, heterovalent dopants also act as scattering centers. Thus, the conductivity exhibits a nonlinear correlation with dopant concentration [41].

In a plasmonic semiconductor system, the Q-factor reaches an upper limit, albeit with increasing doping levels [123,240]. Compensating defects, easily formed at localized surface charges, have an adverse impact on plasmon resonances [268,269]. Those nonionized ions occupying deeper states in the bandgap do not contribute to the plasmon response [24]. Besides, the nonparabolicity of the conduction band at very high carrier density leads to a reduced plasma frequency [24]. From a practical point of view, there is always a compromise of the doping level between the plasmon response and functional needs. For example, progressive doping



Fig. 10. Impact of size and shape on the plasmonic properties of semiconductor nanostructures. (a) The LSPR band influenced by optical retardation effect in nanoparticles of larger diameters. Reproduced with permission [15]. Copyright 2019, De Gruyter. (b) FTIR spectra and (c) relative LSPR shift of $Cr_sSn:In_2O_3$ nanocrystals as a function of particle diameter. Reproduced with permission [46]. Copyright 2019, American Chemical Society. (d) LSPR band transformation of self-doped CdO nanocrystals as a function of their average diameters. The origin of nonstoichiometry and free-carrier generation is sketched in (e). Reproduced with permission [146]. Copyright 2020, American Chemical Society. (f) Near-field intensity distribution in the proximity of sphere-, cube-, and triangle-shaped nanocrystals under excitation at resonant frequencies. Reproduced with permission [275]. Copyright 2017, American Chemical Society. (g) STEM images of an anoxic MOO₂ nanoribbon (top), which was cut into two stripes under high-energiers. Reproduced with permission [118]. Copyright 2020, Wiley-VCH. (h) Experimental reflection data of a VO₂ disk array upon 330–340 °C heating, with enhanced scattering at intermediate temperatures. Reproduced with permission [231]. Copyright 2018, American Chemical Society. (i) Optical hysteresis of VO₂ thin films under incident light radiation of 2.5 µm. Film thicknesses are 100 (solid line) and 400 nm (dashed). Reproduced with permission [231]. Copyright 2018, American Chemical Society.

enhances the free-carrier concentration for plasmon resonance amplification in FICO nanocrystals, but the accompanied optical bandgap widening harms the electrochromic property. Therefore, 3 % of In, F doping in FICO nanocrystals gives rise to the best electrochromic performance within the 0–20 % doping range [147].

4.1.1.2. Dopant distribution. The dopant distribution influences the plasmonic response of semiconductor nanostructures regarding radial distribution and dopant clustering. Here, we focus on the discussion of radial distribution. As sketched in Fig. 8d, the dopant radial distribution encompasses three circumstances: interior accumulation, homogenous distribution, and surface aggregation. In both self-doped [146] and extrinsically doped [126,270] semiconductors, dopants interiorly accumulated govern the LSPR response. Fig. 8e compares the absorption spectra of In_2O_3/ITO and ITO/In_2O_3 core–shell nanoparticles [241]. In the ITO/In_2O_3 core–shell nanoparticles, where the dopants are accumulated in the core, the system renders a lower plasma frequency and a high Q-factor of 7.2. Fig. 8f yields the free carrier concentration (N_e) as a function of doping content. It manifests that to sustain an equivalent LSPR energy, the dopant concentration in the ITO/In_2O_3 nanoparticles is nearly an order of magnitude lower than in the In_2O_3/ITO counterpart. This phenomenon originates from the core accumulation of Sn dopants in ITO/In_2O_3 nanoparticles, where dopants convert from irreducible complexes into mobile Sn⁴⁺. This architecture is also conducive to the suppression of surface impurity scattering.

A surface depletion layer usually comes with interior dopant accumulation. As depicted in Fig. 8g, the surface depletion stems from Fermi-level pinning, where the surface state level sits at an energy lower than E_F . This scenario results in near-surface band bending, diminishing the surface carrier population. The spatial gradient of the carrier concentration reflects the extent of surface depletion (V_{bb}):

$$V_{bb} = E_{F,fb} - E_s, \tag{20}$$

where $E_{F_{fb}}$ and E_S are the flat-band Fermi level and the surface energy, respectively [13]. This depletion layer deteriorates the extinction intensity, hot-carrier transfer and environmental sensitivity of plasmonic nanocrystals [81]. In particular, hot carriers excited in the nanoparticle interior can hardly overcome the energy potential built by the depletion layer. Consequently, short-lived hot carriers are trapped inside nanoparticles and eventually decay. A variety of routes adjusts the depletion width. For instance, surface dopant enrichment narrowed the depletion layer in ITO nanocrystals. Besides, an atomic-thick alumina layer passivated surface depletion as well [271].

On the contrary, under surface aggregation circumstances, surface states play a principal role, including defects, trap states, and surface-bound molecules. Fig. 8h presents the extinction spectra of In_2O_3/ITO core–shell nanostructures, where the shell thickness is highly relevant to the dual-mode plasmonic response [272]. This distinct phenomenon is appealing for sensing applications, as the dual-mode character is highly susceptible to environmental refractive index fluctuations. Furthermore, the electronic coupling can inject hot carriers generated near the surface into the adjacent adsorbates.

4.1.2. Crystalline structure modulation

The crystalline structure of plasmonic semiconductors alters the dopant behavior by changing the coordination environment of dopants in different crystal phases. As shown in Fig. 9a, Ag₂Se colloidal QDs experience distinct peak splitting during nanocrystal growth, which is associated with a structural cubic-to-tetragonal conversion [159]. Similarly, Cu_{2-x}S released substantial copper vacancies during the antifluorite-roxbyite structural transition [33]. This oxidation-triggered transition blueshift the LSPR band without modifying the particle morphology. Yin *et al. in-situ* tailor the oxygen deficiencies by engineering crystal facets of TiO₂ nanocrystals [76]. The plasmonic response differs in ITO nanocrystals with cubic or rhombohedral structures [28]. The Burstein-Moss shift drives the optical bandgap modulation and plasmonic response in the cubic structure. In contrast, band renormalization prevails in the rhombohedral structure, leading to the absence of LSPRs. Plasmon resonances in MoS₂ are attributed to the phase evolution, which is either from 2H to 1 T phases or from semiconducting-MoS₂ to metallic-Li_xMoS₂ [224]. Besides, the crystallinity also affects the plasmonic performance in semiconductors, mainly by trap states and defects around grain boundaries [6]. In plasmonic Ti_{1-x}Mg_xN, the epitaxial (001) phase displays a Q-factor an order of magnitude higher than the polycrystalline layer [114].

In recent years, crystalline anisotropy has drawn much attention for plasmonics, particularly in 2D materials. 2D materials exhibit anisotropic plasmon properties attributed to the anisotropy of band structures and effective masses. Fig. 9a manifests the plasmon dispersion of monolayer phosphorene, where the armchair direction (*x*) reflects a higher resonance frequency due to the smaller band mass [177]. Anisotropic mass approximation provides a band-mass estimation in monolayer phosphorene, where $m_x^* \approx 0.2m^*$ and $m_y^* \approx 1.1m^*$; *x*, *y* being the armchair and zigzag directions, respectively. Fig. 11a reveals two distinct plasmonic bands along the *a* and *b* axes in WTe₂ microdisk arrays, whose sharpness, shape and intensity are highly temperature dependent [48]. Similarly, the crystalline anisotropy in hexagonal Cs:WO₃ nanocrystals results in dual longitudinal and transverse LSPR modes [51].

The structural anisotropy also imposes control over carrier polarization and discrete quantum states in plasmonic semiconductors, spawning the new field of plasmontronics. Plasmonic $TiO_{2\cdot x}$ nanocrystals generate a cyclotron magnetoplasmoic mode when excited by circularly polarized light in a magnetic field [76]. The plasmonic response of the $TiO_{2\cdot x}$ nanocrystals, as determined by oxygen vacancies, is found to be dictated by the dominating crystalline facets. When using TiF_4 as the precursor for synthesis, a {001} crystalline facet plays dominance in $TiO_{2\cdot x}$ nanoplatelets (abbreviated as F-OLAM). $TiO_{2\cdot x}$ prepared from the TiF_4 - $TiCl_4$ precursor (abbreviated as M-OLAM) results in a predominant {101} facet. So does that prepared from $TiCl_4$ (named as Cl-OLAM). Magnetoplasmonic modes are only observable in F-OLAM and M-OLAM nanocrystals, as shown in Fig. 9d. Consequently, under the plasmon-spin-charge interaction, excitonic Zeeman splitting occurs. In the MCD spectra measured at 5 K shown in Fig. 9e, the spectra of F-OLAM and M-OLAM are evidentially different, implying the vital role of dominating crystalline facets in $TiO_{2\cdot x}$ for selective carrier

polarization.

4.1.3. Morphology tuning

4.1.3.1. Size. For bigger particles with a diameter comparable to the effective plasmon wavelength, the optical retardation effect has an impact on the LSPR [273]. Optical retardation implies that the electrostatic approximation breaks down. This effect causes a phase mismatch between the electron oscillations at different parts of the particle due to a different phase of the incident field at those locations. Consequently, the plasmon resonance of the nanostructure experiences a red-shift and high-order multipolar plasmonic modes can be excited. On the other hand, when the nanostructure size shrinks to become comparable to the Bohr radius, the quantum confinement effect comes into play [113,159,201]. The "quantum plasmon resonance" endows semiconductors with additional quantum states, a blue-shifted LSPR frequency, and stronger field confinement from collective plasmonic modes. As shown in Fig. 10a, absorption dominates the resonance interaction in small particles, while scattering plays an overwhelming role in bigger particles.

The nanocrystal size also affects the interparticle plasmon interaction in nanocrystal films. Cr:ITO nanocrystals experience an LSPR band blueshift and sharpening with the particle size expansion caused by Cr incorporation, as shown in Fig. 10b [46]. Fig. 10c reveals a linear correlation between the LSPR peak shifting and the particle diameter under electrochemical charging. Hence, this size effect provides an additional degree of freedom in LSPR controllability. Its origin is plasmon coupling between adjacent nanoparticles, which persists better in larger-radius nanocrystals and at longer interparticle distances. Notably, there is competition and a trade-off between plasmon coupling and surface depletion, which becomes more eminent in smaller nanocrystals with surface potentials lower than the Fermi level. Yan *et al.* observed plasmon hybridization among near-touching TiO_{1.67} nanoparticles, where the plasmonic mode splits into bonding and antibonding modes in the strongly interacting dimer [10]. Therefore, plasmon hybridization allows broadband absorption and hot-carrier generation at multiple energy levels, holding high promise in solar energy harvesting and local heating [10,51]. When nanocrystals are well isolated, interparticle plasmon effects have a marginal influence in such particle suspensions.

The nanocrystal size has an inverse relation with the specific surface area. In self-doped plasmonic semiconductors, the resonance frequency moves inversely with the particle size derived from surface-induced nonstoichiometry. Fig. 10d reveals the modulation of plasmonic response in self-doped CdO nanocrystals across a broad MIR range from 2.4 to 6.0 μ m. As depicted in Fig. 10e, Cd²⁺ ions aggregate on the nanocrystal surface, whereas oxygen vacancies preferentially sit in the interior. Since oxygen vacancies predominantly donate free carriers in CdO nanocrystals, the particle size enhancement suppresses the LSPR energy [146]. Cr:ITO nanocrystals present the same size-dependent tendency, which supports the surface aggregation of irreducible $2Sn_{in}^{*} - O_{i}^{*}$ complexes [126]. In addition, the nanocrystal size also affects the surface scattering of carriers, and hence plasmon damping. Thus, larger nanocrystals synergistically improve semiconductor nanostructures' Q-factor and carrier mobility [126,274].

4.1.3.2. Shapes. The electromagnetic field distribution in plasmonic nanostructures of different shapes but the same volume is plotted in Fig. 10f [275]. The plasmonic field is inhomogeneously distributed in nanostructures other than spheres, sustaining ultra-high field intensity around corners. The localized field confinement and interparticle plasmonic coupling lead to the generation of hotspots [27,72]. These hotspots support an ultra-strong local field in semiconductor nanostructures, even exceeding that in the metal counterparts. Additionally, anisotropic nanocrystals could excite various plasmonic modes along different structural axes depending on the incident light polarization [51,151,276]. Shape-dependent anisotropic plasmonic modes are closely associated with anisotropic effective masses along different crystal axes. This phenomenon is possible in 2D materials. For example, in-plane anisotropic 2D materials like WTe₂ can host anisotropic 2D plasmons and natural hyperbolic plasmon-polaritons [48].

The geometric design of semiconductor nanostructures is capable of regulating the plasmon energy. As shown in Fig. 10g, a long monoclinic MoO_2 nanoribbon breaks into two via bombardment with a focused electron beam in the TEM [277]. The longer one presents distinct quadrupole (0.26 eV) and higher-order (0.30 eV) modes, while the shorter nanoribbon supports dipole (0.22 eV) and quadrupole (0.35 eV) modes. $WO_{2.8}$ nanorods exhibit a similar phenomenon [103]. In addition, a change in the crystal shape provides a means to tune the temperature window for the dielectric-plasmonic transition in plasmonic PCMs. As shown in Fig. 10h, the VO_2 disk arrays present a narrow MIT window of 4 K, witnessing an abrupt reflectivity change [231]. In contrast, the MIT window of VO_2 thin films and wire arrays approaches 20 K, as manifested by the optical hysteresis shown in Fig. 10i.

The aspect ratio quantifies the extent of shape asymmetry, defined as the length-over-width ratio. This metric is defined as the diameter-over-thickness ratio in nanodisks and the inner-outer-diameter ratio in nanoshells. The aspect ratio determines the minimal ε_1 required to launch plasmons in plasmonics. In the quasi-static limit, the plasmon resonance in a sphere occurs when $\varepsilon_1 \leq -2$, while a more negative ε_1 value is required in nanostructures with higher aspect ratios, for instance, in nanorods and nanoshells [6]. Another critical shape factor in plasmonics is the number of surface facets. First, an increase in the facet number leads to broadening and merging the neighboring LSPR bands in Cs_xWO₃ and ICO nanocrystals [33,41,206]. Second, the facet number plays a decisive role in the upper limit of the doping level. In plasmonic ICO nanocrystals, maximal 6 % and 20 % doping levels can be attained in octahedral and spherical shapes, respectively [41]. In practice, the nanocrystal shape is altered by the synthetic conditions [156,278], the reaction precursors [33,124,279], and dopants [72,244].

4.2. Plasmonic semiconductor metasurfaces and self-assemblies

4.2.1. Plasmonic semiconductor metasurfaces

Plasmonic metasurfaces are planar arrays of artificial structures of subwavelength dimensions and spacing. The individual noanounit functions as a plasmonic antenna, inter-converting the near-field oscillating currents and far-field electromagnetic waves [54]. Metasurfaces produce abrupt changes in the phase, amplitude, and polarization of the transmitted, reflected, scattered, or emitted light over a subwavelength scale [52.237.280]. Plasmonic metasurfaces enable complex wavefront engineering and miniaturization of optical components with novel functionalities [47,246]. Plasmonic metasurfaces of ordered arrays can sustain the plasmonic surface lattice resonance [164,279]. This resonance engenders a guided wave propagating along a periodic array, substantially intensifying and sharpening the resonance band [5,27,47,53]. An electrical-grid-controlled active metasurface converts between an individual state of isolated resonance and a collective state of extended resonant interaction, holding high potential for high-speed, broadband frequency modulation [266]. In addition, plasmonic metasurfaces offer more efficient energy conversion for optical control. For example, the VO₂ metasurfaces allow a 30 % improvement in emittance tunability compared to the unstructured film. This metastructure implies a novel optical solar reflector in the NIR region [265]. Metasurfaces consisting of plasmonic semiconductors allow a closer packing of nanoantenna arrays without deteriorating the resonance quality factor. The refractive index of semiconductor metasurfaces can be enormously modulated, especially in the MIR region [163,164]. Thanks to efficient carrier separation, semiconductor metasurfaces also boost the hot carrier conductivity [164]. Hence, based on semiconductor plasmonic metasurfaces, one can envision a smaller device footprint, a higher density of hotspots, and spacially extended plasmonic surface lattice resonance. The exploitation of semiconductor metasurfaces relies decisively on state-of-the-art lithography techniques, including but not limited to, focused ion beam (FIB) lithography, electron beam lithography (EBL), laser interference lithography, nanoimprint lithography, plasma ashing, wet etching, and template-assisted lithography [15,55,232,238,246]. The most common plasmonic metasurfaces consist of nanorods due to their fabrication simplicity and extreme field enhancement for spectroscopic sensing. Fig. 11a displays degenerate perovskite (Ba,La)SnO₃ nanorods of similar cross sections but different aspect ratios [281]. The plasmon resonance of these rectangular rods manifests in the EELS spectra in Fig. 11b. The aspect ratio negatively correlates with the plasmon energy and the bandwidth, which is associated with the strong resonance in the dipolar modes.



Fig. 11. Plasmonic semiconductor metasurfaces and nanocrystal self-assemblies. (a) STEM images of La-doped $BaSnO_3$ nanorods with different aspect ratios. Reproduced with permission [281]. Copyright 2022, Wiley-VCH. (b) EELS spectra of the La-doped $BaSnO_3$ nanorods, in which the curve colours match with the cross markers in (a). Reproduced with permission [281]. Copyright 2022, Wiley-VCH. (c) Schematic of a Si:InAs/AlSb hyperbolic metamaterials embedded with InAs quantum wells. Reproduced with permission [222]. Copyright 2021, American Chemical Society. (d) Real and imaginary permittivity of the Si:InAs/AlSb HMMs, demonstrating the type-I HMMs, type-II hyperbolic metamaterials and intersubband transition regions. Reproduced with permission [222]. Copyright 2021, American Chemical Society. (e) Optical microscopy and SNOM images of two antenna areas, where Antenna 1 is surrounded by the monoclinic metallic VO₂ phase, while Antenna 2 is surrounded by the as-grown monoclinic insulating phase. Bottom: optical microscopy and SNOM images, with the monoclinic metallic phase erased around Antenna 1 and patterned around Antenna 2. Scale bar: 2 μ m. Reproduced with permission [117]. Copyright 2020, American Chemical Society. (f) SEM image of self-assembled plasmonic chestnut-like WO_{2.72} superlattices. Reproduced with permission [260]. Copyright 2017, American Chemical Society. (g) Cu₂O cube-like superstructures (bottom). Reproduced with permission [120]. Copyright 2018, Wiley-VCH.



Fig. 12. Plasmonic properties modulated by electrochemical biasing in semiconductor nanostructures. (a) Mechanistic demonstration, band structures and LSPR band evolution of FICO nanocrystals under electrochemical biasing. Reproduced with permission [147]. Copyright 2019, American Chemical Society. (b) Extinction spectra of Cr, Sn-codoped In_2O_3 nanocrystals upon stepped electrochemical biasing from +2.0 V to -1.5 V at Cr doping content of 0 % (left) and 20 % (right). Reproduced with permission [46]. Copyright 2019, American Chemical Society. (c) Top: electrochemical (de)lithiation of Cu_{2-x} Se nanocrystals. Bottom left: electrochemically charged voltage as a function of the time for absorption measurements. Bottom right: LSPR absorption spectra of Cu_{2-x} Se nanocrystals measured at the time points shown in the left image. Reproduced with permission [157]. Copyright 2018, American Chemical Society. (d) Left: simulated crystal structure of $Cu_{1.75}$ Se charge rearrangement after Li insertion. Right: $Cu_{1.75}$ Se band structures before and after ion intercalation. Reproduced with permission [157]. Copyright 2018, American Chemical Society. (e) Tansmission spectra of Nb:TiO₂ nanocrystals at bias voltages of 0 V (blue), -3 V (green) and -4 V (red). Reproduced with permission [247]. Copyright 2017, American Chemical Society. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

In the recent decade, innovative functionalities have been explored in plasmonic semiconductor metasurfaces. Semiconductorbased hyperbolic metamaterials accommodate anisotropic volume plasmon polaritons with an enormous optical LDOS [48,177,222]. Fig. 11c depicts an epitaxial Si:InAs/AlSb hyperbolic metamaterial [222]. The intersubband transition occurs in the InAs/AlSb quantum well. The hyperbolicity arises from the coupling of SPPs and the cavity mode at the metallic-dielectric interface. The real and imaginary permittivity shown in Fig. 11d reveals the coexistence of type-I ($\varepsilon_{\parallel} > 0$ and $\varepsilon_{\perp} < 0$), type-II hyperbolic metamaterials ($\varepsilon_{\parallel} < 0$ and $\varepsilon_{\perp} < 0$) and an intersubband transition at 14 µm. The hyperbolic metamaterial offers tempting opportunities for quantum entanglement and single emitters. Programmable plasmonic metasurfaces are another promising development, especially in PCMs. VO₂ nanowire arrays have accomplished dynamic and reversible thermal tuning between plasmonic and dielectric Mie resonances [117,231,238]. This phase conversion in VO₂ also causes switchable hotspots, as shown in Fig. 11e [117]. VO₂ is initially an insulator while converting into a metallic phase by scanning a biased AFM probe at room temperature. Remarkably, the rectangle of the metallic phase is erased at high temperatures (>348 K), and can be repatterned. This programmable VO₂ transition allows spatial plasmonic modulation, reversibly switching the hotspots in antennas. The VO₂ MIT can also be thermally activated at 25 °C around 5-nm nanogaps [282]. The reconfigurable metasurfaces are therefore enticing for smart windows, energy harvesting, and active nanophotonics devices [14,15,49].

4.2.2. Plasmonic semiconductor self-assemblies

The semiconductor nanocrystal self-assembly offers another pathway to obtain highly periodic and homogeneous plasmonic platforms without much artificial design. The selection of organic ligands is critical in determining the hydrophobicity of colloidal nanocrystals. Thanks to these ligands, plasmonic nanocrystals homogeneously disperse in the solvent and then arrange into a uniform, well-ordered film after natural drying [127]. The plasmonic nanocrystal assemblies render a longer-range plasmonic interaction,



Fig. 13. Plasmon tuning by electrostatic and photochemical doping in semiconductor nanostructures. (a) Plots of real and imaginary parts of the permittivity in plasmonic semiconductors of the epsilon-near-zero (ENZ) performance with and without an external electric field. Reproduced with permission [239]. Copyright 2018, Optica Publishing Group. (b) 3D carrier density profile of the ion-gel-gated β-Ga₂O₃ thin film under different gating voltages (V_g) at 300 K. Inset: accumulation layer thickness as a function of V_g. Reproduced with permission [71]. Copyright 2022, American Chemical Society. (c) Band structure of FICO nanocrystals upon intraband (1350 nm) and interband (400 nm) pumping. Reproduced with permission [286]. Copyright 2016, American Chemical Society. (d) Two-dimensional $\Delta T/T$ mapping under intraband and interband pumping as a function of pump–probe delay and probe wavelength. Reproduced with permission [286]. Copyright 2016, American Chemical Society. (e) Band structure variation during ITO photodoping, and evolution of the absorption spectra of ITO and In₂O₃ nanocrystals under increasing UV exposure. Reproduced with permission [287]. Copyright 2015, American Chemical Society. (f) Optical images of an α-MoO₃ flake suspension after solar light radiation for 0–5 h, and corresponding UV–visible absorbance spectra. Reproduced with permission [191]. Copyright 2014, Wiley-VCH.

higher plasmon tunability, stronger mechanical robustness, and easier integration into optical devices. In addition, self-assemblies act as an effective medium for designing the anisotropic plasmon behavior. Self-assembled TiO_{2-x} nanocrystals exhibit anisotropic plasmon response, which is ascribed to the deviation of effective masses along different axes in the anatase structure of TiO_{2-x} [151]. Anisotropic $Cu_{2-x}S$ nanodisks stack in a face-to-face or side-by-side geometry, depending on the ligand hydrophobicity [33]. Recently, self-assembled plasmonic 3D superlattices or clusters have been developed [41,113]. For instance, Fig. 11f showcases $WO_{2.72}$ chestnutlike 3D nanostructures [260], while Fig. 11g displays Cu_2O cube-like superstructures [120].

4.3. Post-synthetic engineering of plasmonic properties

The insufficient free-carrier density has been a long-existing bottleneck for plasmonic semiconductors, which causes thermodynamic dopant solubility, dopant compensation, and carrier trapping. Post-synthetic tuning methods provide remedies to this issue. This section elaborates on possible routes via altering the redox equilibrium, surface coordination, and reversible post-synthetic doping.

4.3.1. Electrochemical modulation

When applying an electrochemical bias, a film or particle assembly of plasmonic semiconductors generates excess free carriers, generally implemented in an electrochemical cell. Fig. 12a depicts the working principle of electrochemical processes by taking the FICO nanocrystal film as an example [147]. When subjected to negative bias (in the ON state), the FICO nanocrystals experience the electron injection and attraction of Li⁺ ions from the electrolyte. The charge transfer between FICO and surface-attached Li⁺ ions essentially alters E_F or μ of FICO. E_F regulates the free-carrier concentration and hence the plasma frequency [127], whereas μ engineers the amplitude of the resonance peak [283]. As indicated by the band diagrams and absorption spectra, the electrochemical

charging elevates E_F and widens the optical bandgap, leading to the blueshift and amplification of the LSPR band. This pseudocapacitive surface reaction allows a 1200 nm frequency shift and a 3-fold intensity variation in ITO nanocrystals [127]. By covalent linking with amorphous niobium oxide glass (NbO_x) and manipulating the surface depletion, the plasmonic performance of ITO nanocrystals was further enhanced and engineered [13,284]. Capacitive charging has also been applied in a wealth of materials such as Cr:ITO [46], ATO [4], or anatase TiO₂ [151]. Several factors influence the extent of plasmon modulation during capacitive charging. Fig. 12b manifests the impacts of the doping content in Cr,Sn:In₂O₃ nanocrystals [46]. During the reverse charging cycle from +2.0 V to -1.5 V, the shift of plasmonic peaks varied from 420 cm⁻¹ in nanocrystals without Cr doping to -240 cm⁻¹ in 20 %-Cr-doped Cr,Sn: In₂O₃. The plasmon tailoring during the capacitive charging can also be influenced by (i) the active volume of nanoparticles and (iii) interparticle interactions [46]. Pure capacitive charging, with a robust, instantaneous, and reversible alteration of plasmon behavior, is usually achieved using electrolytes with bulky and nonintercalating cations, such as tetrabutylammonium bistrifluoromethanesulfonimidate (TBA).

Under electrochemical biasing, other reactions, such as phase transformation and carrier trapping, may occur simultaneously, which derive from the insertion of small cations such as H^+ and Li^+ . Fig. 12c depicts a Faradaic redox reaction of Cu_{2-x} Se nanoparticles in the electrochemical cell, causing (de)lithiation during (de)charging [157]. Under negative biasing, the LSPR band gradually redshifts and is suppressed, demonstrating excellent cyclic stability and reproducibility. As indicated by the numerical study in Fig. 12d, the guest lithium atoms preferentially accommodate at the copper vacancies in Cu_{2-x} Se nanoparticles. The lithium-ion intercalation does not affect the band shape but pronouncedly lifts E_F . By virtue of the capacitive charging and ion intercalation, plasmonic Nb:TiO₂ nanocrystals present a dual-band electrochromic response [247]. As shown in Fig. 12e, within the 0–3 V voltage window, the Nb:TiO₂ transmission spectrum (green) shows a broadband visible-NIR transmittance stemming from enhanced localized surface plasmon scattering. Via external biasing from 3 V (red curve) to 4 V (blue), the layer transmittance decreases significantly in the visible region due to enhanced plasmon extinction from Li intercalation. The impact of Li treatments on the plasmonic properties is mainly attributed to defect engineering, lattice distortion, structural transformation, and interlayer gap expansion in semiconductors [87,262]. In addition, the electrochemical Li intercalation of MoS₂ flakes gives rise to a near-UV–visible plasmonic response Semi-metallic states formed during the surface phase transition explain this scenario [177,224].

4.3.2. Electrostatic and photochemical charging

In plasmonic semiconductors, electrostatic charging is an effective way to shift the ENZ point, where $Re[\epsilon(\omega)]\cong 0$. Fig. 13a plots the relationship between the permittivity and the ENZ point in a plasmonic CMO under both biased and unbiased conditions [239]. The ENZ point is significantly blue-shifted by applying a gate voltage. This phenomenon stems from the electrostatically tuned free carrier concentration, giving rise to a carrier accumulation layer under biasing. Thus, the material system exhibits metallic and dielectric properties at the same incident wavelength, serving as two states in modulators [24,128]. Rajapitamahuni *et al.* studied the dependence of the thickness of the carrier accumulation layer in electrostatically gated β -Ga₂O₃ films [71]. As shown in Fig. 13b, the film mobility elevates significantly by electron accumulation under positive gating in an ion-gel-gated transistor. Along the thickness of the film, where z = 0 denotes the Ga₂O₃-substrate interface, the thickness of the carrier accumulation layer (denoted as d_A) is negatively dependent on the gate voltage via varying the 3D carrier density profile (n^{3D}) .

Photodoping — an above-bandgap photoexcitation process — modifies plasmonic properties through capacitive charging, as essentially different from chemical doping [269,285]. To reveal this difference, Kriegel *et al.* carried out a plasmon dynamics study in FICO nanocrystals [286]. As sketched in Fig. 13c, pumping at 400 nm causes interband excitation driving photodoping. Pumping at 1350 nm induces intraband excitation and dominates the LSP excitation. Fig. 13d presents the differential transmission $\Delta T/T$ maps obtained from the TA spectroscopy. Photodoping at 400 nm experiences a monoexponential decay, followed by an ultrafast increase of carrier densities to allow active LSPR control as well as plasmon damping [6]. At 1350 nm pumping, the LSPs excited from chemically-doped dopants decay in two steps, namely: (i) local carrier heating and thermal dissipation towards the lattice; (ii) excitation of the radial breathing mode.

Photochemical charging is highly susceptible to oxidation, where the dopant ions bind more tightly with protons than the host lattice [269]. Therefore, photodoping is mostly employed under anaerobic conditions. This protocol enables the plasmon modulation to the extent that is unattainable via *in-situ* chemical doping. Fig. 13e explains the photodoping-affected plasmon resonance in In₂O₃ and ITO nanocrystals, where ethanol acts as a sacrificial reductant for electron accumulation around the CBM [287]. Fig. 14a reveals a progressive enhancement in the LSPR intensity for both In₂O₃ and ITO nanocrystals under UV radiation. The process is reversible by air exposure or the addition of mild oxidants, such as $[FeCp_2^*]^+$. In 2D materials, ion intercalation also contributes to photochemical charging. As shown in Fig. 13f, intrinsic 2D α -MO₃ exhibits no LSPR response, while α -MO_{3-x} flakes produce highly tuneable LSPs under solar light radiation [191]. With elongation of the radiation duration, the extinction bands witness a gradual blueshift and intensification, as well as an evident color evolution of the α -MO_{3-x} suspension. During light exposure, massive oxygen deficiencies in α -MO₃ create intermediate H_xMoO₃. Then, the degeneration of long Mo-OH₂ bonds in H_xMoO₃ gives rise to stable and nonstoichiometric states of MoO_{3-x} phases. The α -MO₃ photodoping profits from (i) its high permittivity, (ii) depolarization factor, and (iii) high tolerance to massive intercalating ions.

The photodoping effect can be preserved in semiconductors in the long term by altering the dopant compensation mechanisms. In degenerate Ga:ZnO nanoparticles, electrons, Zn vacancies and oxygen interstitials compensate for excess charges from Ga doping. When dispersing the nanocrystals in a hole-scavenging medium such as n-butanol, the delocalized electrons in the conduction band dominate the carrier compensation under UV radiation [142]. Owing to this preferential compensation mechanism, the photodoping effect persists for months in the ambient circumstance, maintaining a long-term enhanced LSPR in Ga:ZnO nanoparticles. Besides, the defect states within the bandgap also exert impacts on photodoping. During photodoping with UV radiation of Fe:ZnO nanocrystals, the induced electrons tend to fill in-gap states before reaching the CBM for the LSPR excitation [143]. As a result, photodoping initially gives rise to the reduction of the substitutional dopant Fe_{Zn}^{3+} and interstitial dopant Fe_{int}^{3+} , followed by the subsequent LSPR. This *ex-situ* charge transfer process can be recovered upon air exposure, providing an opportunity for reversible ferromagnetism.

4.3.3. Ligand exchange

Semiconductors are usually covered with rich coordination sites, dangling bonds and surface trap states, the latter two of which are generated from incomplete passivation of surface atoms. These surface states exert a nonnegligible influence on the plasmonic properties. Ligand exchange is a substitution reaction, imposing surface passivation, surface charge balancing, and hydrophobicity adjustment [4,33]. Fig. 14a schematically explains the surface passivation of WO_{3-x} nanoplatelets via ligand exchange, which is implemented by adding tetradecylphosphonic acid (TDPA) [197]. The ligand passivating the WO_{3-x} surface is the phosphonate-binding head group. The band diagram illustrates the passivation of shallow traps around the CBM and the transfer of trapped electrons into the conduction band after the TDPA treatment. The TDPA-induced ligand exchange elevates the free-carrier density to 8.4×10^{22} cm⁻³. Besides, the phosphonate binding head group coordinates with three neighboring W atoms with moderate bond length to bypass steric hindrances. Thus, the plasmon behavior alters accordingly in TDPA-treated WO_{3-x}, giving rise to an unprecedented bulk refractive index sensitivity of 428 RIU/nm, as shown in Fig. 14b.



Fig. 14. Ligand exchange and other redox reactions in plasmonic semiconductors. (a) Left: $WO_{3\cdot x}$ nanoplatelets covered with alkyl phosphonate groups. Right: conduction-band filling and carrier transfer in $WO_{3\cdot x}$ nanoplatelets via the tetradecylphosphonic acid (TDPA) treatment. Reproduced with permission [197]. Copyright 2022, American Chemical Society. (b) Relationship between the peak positions of LSP bands and the refractive index of the pristine (black) and TDPA-treated (blue) $WO_{3\cdot x}$ nanoplatelets. Reproduced with permission [197]. Copyright 2022, American Chemical Society. (c) Cation exchange between CuCl₂ and ICO nanocrystals. Reproduced with permission [293]. Copyright 2019, Springer Nature. (d) Absorption spectra of Cu-doped ICO (Cu:ICO) nanocrystals measured after 0–120 min cation exchange reactions [293]. Copyright 2019, Springer Nature. (e) Absorption spectra of pristine ICO nanocrystals, pristine Cu:ICO nanocrystals, and Cu:ICO nanocrystals reacted with In(ac)₃ at 150–250 °C. Reproduced with permission [293]. Copyright 2019, Springer Nature. (f) Schematic of various redox-active molecules interacting with plasmonic nanostructures. Reproduced with permission [294]. Copyright 2015, Wiley-VCH. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 15. Heterogeneous plasmonic semiconductors. (a) SEM images of TiN nanoparticle arrays and a TiN/VO₂ film consisting of TiN nanoparticles and VO₂ coating. Reproduced with permission [162]. Copyright 2018, Wiley-VCH. (b) Transmission spectra of the TiN/VO₂ film measured at 20 and 80 °C, showing a NIR switching efficiency of 48 %. Reproduced with permission [162]. Copyright 2018, Wiley-VCH. (c) Energy dispersive spectroscopy (EDS) mapping in TEM of Cu_{2-x} Se-Au (CSA) nanoparticles. Reproduced with permission [11]. Copyright 2019, American Chemical Society. (d) LSPR absorption spectra of CSA (red) and Cu_{2-x} Se (black) nanocrystals. Reproduced with permission [11]. Copyright 2019, American Chemical Society. (e) LSPR extinction spectra of Au nanorods and their hybrids with core–shell Cu_7S_4 -Au heterostructures. Reproduced with permission [296]. Copyright 2018, Wiley-VCH. (f) Simulated local electric field distribution in core–shell (left) and dumbbell-like (right) Cu_7S_4 -Au heterostructures. Reproduced with permission [296]. Copyright 2018, Wiley-VCH.

Aside from surface passivation, high-order plasmonic modes are generated through coupling between the fundamental plasmonic mode and the molecular vibration of capping ligands. For example, in F-doped ITO nanoparticles, a Fano-type interference results in an asymmetric extinction band with the coexistence of a broad LSPR band and a sharp peak of ligand molecule vibration [72]. In addition, the ligand-induced surface functionalization is able to alter the nanocrystal shape, stabilize the nanocrystal suspension, tune the medium permittivity, facilitate nanocrystal self-assembly and expand the plasmonic functionality [28,241,250]. Ligands, including methoxy poly (ethylene glycol) (mPEG), oleic acid and Tween 20 are widely employed. They present a high potential for bio applications due to their biocompatibility, physiological stability, water dispersity, and blood retention [12,69,104,105,190]. Polyvinylpyrrolidone (PVP) also provides surface coordination that effectively promotes the dispersion of MoO_{3-x} nanobelts in water, phosphate-buffered saline (PBS) buffer and cell-culture medium [248].

Ligand exchange in semiconductors imposes dielectric-to-plasmonic conversion via two routes: (i) to exchange the capping ligands and (ii) to remove the capping ligands to make "naked" plasmonic nanostructures. The ligands of 1,2-ethanedithiol (EDT) and formic acid (FA) significantly elevate the conductivity of ITO nanocrystals [288]. The "naked" FICO nanocrystals are produced by replacing the native ligands of insulating oleic acid (OA) with FA, which was then removed by annealing at 250 °C for 1 h in an argon atmosphere [147]. These FICO nanocrystals exhibited nearly metallic conductivity to support strong LSPRs, with a carrier concentration of 7.67 $\times 10^{20}$ cm⁻³.

4.3.4. Other redox reactions

Redox reactions regulate the optical absorption and losses of as-prepared plasmonic semiconductors via deliberately inducing redox-active species. Hence, these reactions enable the tuning of free-carrier densities, rearrangement of the lattice and better activation of dopants [24]. Among them, ion exchange and post-annealing are widely investigated for *ex-situ* modulation of plasmon properties. Ion exchange mostly occurs in colloidal semiconductor nanoparticles, replacing ions in the lattice with guest ions with the structural reorganization [289]. Post-synthetic cation exchange is harnessed more frequently to tailor carrier dynamics and plasmonic responses in semiconductors, as the smaller cations move faster than anions [290]. During the ion exchange transformation, the redox reaction takes place at the nanoparticle surface according to the relative reduction potential between the host and guest ions, followed by ion diffusion. Hence, absorption or desorption of the net charge modifies the free-carrier concentration, leading to a plasmon energy shift [33,289–292]. This process allows plasmonic tuning to an extent unattainable in conventional as-synthetized chemical doping. Liu *et al.* establish a dynamic model describing a programmable LSPR in in ICO nanocrystals via dual-step cation exchange reactions [293]. As shown in Fig. 14c, in the first step, *p*-type Cu⁺ dopants, obtained from the instant reduction of Cu²⁺ in CuCl₂ solution, were added into the *n*-type CdO lattice. As shown in Fig. 14d, the dopant compensation causes a ~ 76 meV redshift of the LSP energy within 30 s of the redox reaction. The second process, Cu⁺/Cd²⁺ exchange, further augments the n-doping, allowing a substantial blueshift of the LSPR energy.

The post-annealing reactions allow redox reactions between the plasmonic semiconductors and a wealth of material systems in



Fig. 16. Semiconductor plasmonic nanostructures integrated with porous frameworks. (a) Fabrication of nanohybrids composed of metal–organic frameworks (MOFs) and plasmonic nanoparticles (NPs). Reproduced with permission [113]. Copyright 2021, American Chemical Society. (b) SEM image of core–shell nanoparticles with Cu_7S_4 on a zeolitic-imidazolate framework (ZIF-8) ($Cu_7S_4@ZIF-8$). Reproduced with permission [299]. Copyright 2016, Royal Society of Chemistry. (c) Absorption spectra of nanoparticles composed of Cu_7S_4 (green), ZIF-8 (black), and $Cu_7S_4@ZIF-8$ (red). Reproduced with permission [299]. Copyright 2016, Royal Society of Chemistry. (d) Surface temperature increase of Cu_7S_4 (circles) and temperature sensor with a Yb³⁺ complex (squares) under 1450 nm laser illumination at different intensities. Reproduced with permission [299]. Copyright 2016, Royal Society of Chemistry. (e) Nanoporous silicate matrix (NSM) embedded with PbS QDs and Cu_2_x Se plasmonic nanocrystals (PNCs). Reproduced with permission [64]. Copyright 2018, Wiley-VCH. (f) Absorption (black) and PL (red) spectra of PbS QDs in the NSM and absorption spectrum of Cu_2_x Se plasmonic nanocrystals in the NSM. Reproduced with permission [64]. Copyright 2018, Wiley-VCH. (g) Schematic illustration of the fabrication of a $MoS_2@TiO_2$ heterostructure. Reproduced with permission [110]. Copyright 2018, Royal Society of Chemistry. (h) Absorption spectra of heterostructures of TiO_2 nanoparticles and different Mo elementary substances and compounds. Reproduced with permission [110]. Copyright 2018, Royal Society of Chemistry. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

oxidizing or reducing ambient, including inorganic or organic molecules, live bacteria and biomacromolecules, as depicted in Fig. 14f [294]. Annealing in an air atmosphere incorporates oxygen into the lattice. Annealing of WO_{3-x} nanocrystals at 175 °C in air leads to the depopulation of free carriers and a redshift and quenching of the LSPR band. A reversed tendency in LSPR modification was observed in WO_{3-x} by the incremental addition of hydrazine as the reducing agent [51,103]. Conversely, Ke *et al.* observed an increased density of O vacancies in the Mg/W-doped VO₂ nanoparticle arrays when annealed at 500–750 °C in Ar atmosphere, which is associated with the promoted LSPR energy and Q factor, as well as a narrowed FWHM of plasmon bands [232].

4.4. Plasmonic engineering in semiconductor heterostructures

4.4.1. Plasmonic semiconductor heterostructures

Semiconductor heterostructures offer several levers to manipulate the plasmonic characters: (i) combining the strength of individual components, (ii) compensating for the shortages of each, (iii) breeding novel surface phenomena, and (iv) facilitating charge separation at the hetero-interface. More intriguingly, some semiconductor heterostructures are indispensable components in active devices, such as the light harvester in photodetectors or the optical gain medium in lasers. These heterostructures could simultaneously serve as plasmon hosts after degenerate doping, simplifying device architecture and fabrication processing, especially for integrated photonics [168,295]. Fig. 15a shows a plasmonic VO₂ film coated with TiN nanoarrays, in which the nitridation of TiO_x forms TiN [162]. The phase evolution during nitridation gives rise to a distinct LSPR absorption band in the NIR region in the TiN nanoarrays. Together with the MIT behavior of the VO₂ coating, this TiN/VO₂ hybrid film confers an excellent IR switching ability ($\Delta T = 48$ %) and



Fig. 17. Semiconductor plasmonics in photonic integrated circuits (PICs), waveguides and light sources. (a) Sketch of a PIC chip. Reproduced with permission [300]. Copyright 2019, Springer Nature. (b) Band alignment of GaSb/InAs (top) and AlSb/InAs/AlSb (bottom) heterostructures. Reproduced with permission [168]. Copyright 2011, Optica Publishing Group. (c) Normalized power flux of GaSb/InAs (top) and AlSb/InAs/AlSb (bottom) dual heterostructures. Reproduced with permission [168]. Copyright 2011, Optica Publishing Group. (c) Normalized power flux of GaSb/InAs (top) and AlSb/InAs/AlSb (bottom) dual heterostructures. Reproduced with permission [168]. Copyright 2011, Optica Publishing Group. (d) Cross-sectional schematic of hybrid photonic–plasmonic (HPP) TiN waveguide epitaxially grown from the sapphire substrate. Reproduced with permission [295]. Copyright 2018, American Chemical Society. (e) SEM image of the HPP waveguide. Reproduced with permission [295]. Copyright 2018, American Chemical Society. (g) Schematic of a GaSa/GaN plasmonic waveguide (left); electric field intensity profiles of the dielectric slot mode (middle) and plasmonic gap mode (right). Reproduced with permission [171]. Copyright 2013, Optica Publishing Group. (h) Working principles of plasmonic lasers. Reproduced with permission [61]. Copyright 2020, Springer Nature.

a high transmittance in the visible-light region (up to 51 %), as revealed in Fig. 15b. Emerging vdW heterostructures provide enticing opportunities for plasmonic devices. These atomically thin hybrid platforms support a fully planar geometry and unique functionalities [20,177]. The heterostructure of graphene stacked with h-BN forms a hyperbolic vdW metamaterial. This vdW heterostructure exhibits ultrahigh plasmon lifetime and field confinement owing to the hybridization of SPPs and hyperbolic phonon polaritons in h-BN [177].

The mixtures of plasmonic semiconductors and metal nanocrystals are also widely investigated, where semiconductors act as complementary for NIR LSPRs. These heterostructures usually work as photocatalysts and photothermal therapy agents [109,260,296,297]. Fig. 15c illustrates dumbbell-shaped Cu_{2-x}Se-Au nanocrystals by energy dispersive spectroscopy (EDS) mapping. Compared to the pristine Cu_{2-x}Se, the hybrids yield the emergence of the Au LSPR band while weakening the Cu_{2-x}Se band (Fig. 15d) [11]. The hybrid suspension features a high photothermal conversion efficiency, witnessing a 44.5 °C temperature increment within 10 min. Similar collective LSPR modes, as revealed in Fig. 15e, were observed in Cu₂S₄-coated Au nanorods with core–shell and dumbbell-like shapes [296]. According to numerical studies and experimental observations, the Cu₂S₄ coating effectively enhances the photothermal conversion efficiency. The simulated field distributions in Fig. 15f reveal a higher local field enhancement on the

dumbbell-like heterostructures than on the core-shell ones. The improvement in plasmonic photothermal conversion primarily originates from (i) an intensified localized field; (ii) suppressed scattering loss; (iii) induced optical absorption at the heterointerface. These plasmonic nanohybrids underpin catalysis applications and trace-amount detection in a rapid, on-site, recyclable fashion.

4.4.2. Plasmonic semiconductors decorated in porous frameworks

Owing to the extremely shallow plasmon penetration depth, the plasmonic applications are hindered by the small plasmon interaction volume, especially in systems containing non-adsorbing molecules or low concentrations of analytes [113]. Plasmonic nanostructures are incorporated into porous frameworks to improve surface affinity and the plasmon-analyte interaction [42]. Possible frameworks include metal–organic frameworks (MOFs), nanoporous matrixes, and nanocavities. The combination of nanoparticles and MOFs (NP-MOFs) has been a dominant presence.

MOFs are a series of 2D materials constructed by organically linked clusters or excess coordination of metal ions [113]. MOFs are favorable frameworks for plasmonic nanoparticle fixation due to their unprecedented specific surface areas (>10000 m²g⁻¹), actively tunable pore sizes, and a large diversity of structures and source materials. There are typically two protocols to attain NP-MOF platforms, as depicted in Fig. 16a. One method is to grow the MOF shell, where the MOF precursor is encapsulated onto plasmonic nanoparticles and eventually nucleates and grows to form MOF shells. The other approach is to decorate plasmonic nanoparticles onto or inside porous MOFs, which is implemented by the reduction reaction of the metallic salt nanoparticles on the MOF surface. The core–shell nanostructures prevail due to their easy fabrication, high photostability, and booming development [113,298,299]. Fig. 16b illustrates core–shell heterostructures with Cu₇S₄ spheres embedded in zeolitic imidazole framework-8 (ZIF-8) [299]. Compared to the pristine Cu₇S₄, the Cu₇S₄@ZIF-8 hybrids intensify the plasmon resonance, as shown in Fig. 16c. The Cu₇S₄-ZIF-8 composites validate a significantly enhanced plasmon-induced local heating (Fig. 16d) and boosted catalytic activity. Similarly, when H_xMoO₃ assembles with iron MOFs (FeMOFs), the core–shell nanostructure remarkably improves the photobleaching and gas sensing performance [298]. Hence, the NP-MOF nanostructures offer attractive opportunities for enhanced spectroscopic sensing, drug delivery, and in-situ tracking and driving chemical reactions and molecular interactions.

The nanoporous silicate matrix (NSM) enables a high-density, non-aggregable loading of nanostructures while maintaining optical transparency. Fig. 16e depicts an NSM decorated with PbS QDs and $Cu_{2-x}Se$ semiconductor plasmonic nanocrystals, which play the role of luminescent and plasmonic sources, respectively [64]. PbS QDs and $Cu_{2-x}Se$ plasmonic nanocrystals are well separated to prevent PL quenching; at the same time, they are placed close enough for near-field interaction. As a result, the PL spectrum of the hybridized system, as shown in Fig. 16f, experiences signal enhancement, band broadening, and resonant frequency shifting. The signal amplification originates from near-field enhancement, whereas the band broadening and shifting are attributed to Rabi splitting and trap-state-associated luminescence. Nanocavities support a similar function in which embedding plasmonic units. Fig. 16g sketches the laminated MoS₂ residing on the sidewalls of TiO₂ nanocavities (MoS₂@TiO₂), which is fabricated in three steps: (i) anodization, (ii) physical vapor deposition, and (iii) chemical vapor deposition [110]. These highly-ordered hybrids exhibit a near-UV-visible tunable localized resonances (Fig. 13h), underpinning a regulated charge separation and transfer pathway and high conductivity of hot electrons.

5. Applications

Highly doped semiconductors have profound practical implications in plasmonics albeit with their relatively lossy nature. Degenerate semiconductors are promising in active plasmonic devices, which confer a negative real-part permittivity for near-field enhancement and potentially low losses for long-distance plasmon propagation. Conversely, scientific efforts are also devoted to making use of the plasmon damping in semiconductors breeding the fields of hot-carrier-assisted catalysis, water treatment, thermochromic smart windows, and thermal therapy. The broad plasmonic band of semiconductors favors applications in biology and solar energy harvesting in contrast with those demanding a narrow-band plasmonic interaction, such as lasers. In addition, the ultrahigh tunability of plasmons in semiconductors, especially the post-synthetic tailoring strategies, supports a dynamic and reversible plasmonic response. This unique plasmonic response is feasible for smart windows, photocatalysis, magnetic recording, and electronic or optical switching applications.

The broadband plasmon frequency in semiconductors overlaps several optical telecommunications bands, solar energy spectrum, and biological transparency window. Besides, semiconductors embrace inherent advantages of source abundance, CMOS compatibility, photocatalytic activity, high physiological stability, and other exotic phenomena to combine with the plasmonic interaction. This section will survey the ever-expanding applications of plasmonic semiconductors, focusing on the platforms of nanocrystals, heterostructures, and metasurfaces. The discussion will highlight the realms of integrated photonics, solar energy, sensing, and bio applications.

5.1. Plasmonic integrated photonics

Photonic integrated circuits (PICs) allow on-chip generation, transmission and processing of photonic signals. By using mature CMOS infrastructures, PICs demonstrate high device compactness, low cost, low power consumption and mass production. Besides, PICs retain the merits of a conventional photonic system, such as high speed, low power consumption, broad bandwidth and high noise resistance [24,144,219]. An even more complex interferometric system, the programmable PIC, has been proposed to achieve spatial redistribution and rerouting of light via complex architectures and algorithms [59]. Therefore, a programmable PIC supports dynamic signal processing with self-adaptation and self-configuration. Fig. 17a depicts the basic architecture of a PIC [300]. In a PIC, the active

components, mainly light sources, electro-optic modulators, and photodetectors, are connected by waveguides and passive components, including beam couplers, beam splitters, optical switches and the optical filters [57,175,182,219,301]. Nowadays, PICs offer enticing opportunities for optical communications, quantum and neuromorphic computing, biological sensing, and environmental monitoring.

A plasmonic PIC converts optical signals to surface plasmons in a PIC, or couples a plasmonic mode with the electromagnetic field propagating in a PIC. Due to the ability to overcome the diffraction limit, a plasmonic PIC renders smaller device footprints, higher bandwidth, lower power efficiency for data throughput, and ultra-high on-chip detection sensitivity [302]. So far, metal-based plasmonic components remain the most widely exploited in plasmonic PICs. Nevertheless, they hinder long-distance signal propagation due to ohmic damping, leaky radiation, defect scattering, and end-facet mirror losses [2,16,303]. To circumvent this issue, one attempt is to coat a dielectric waveguide or an active device with a plasmonic metal surface. This hybrid structure enables the plasmon-photon coupling, simultaneously reaching the deep-subwavelength mode confinement and a sufficient photon propagation distance. So far, this metal-semiconductor hybrid geometry has been exploited in PIC components such as metal/insulator/metal (MIM) slab waveguides [16,20,304], a plasmonic Ag-dielectric MgF₂-CdS nanowire laser [62], hybrid plasmonic modulators including Mach–Zehnder interferometers and ring resonators [140,144,305], and plasmonic grating couplers [2,16]. An alternative solution is to compensate for the plasmon loss by optical pumping [306].

Plasmonic semiconductors have come into play for PIC applications, especially those with (i) plasmon frequencies overlapping with the telecommunication band and molecular fingerprints, (ii) attainable negative real-part permittivity, and (iii) manageable low-loss in the NIR-MIR region. Two classes of plasmonic semiconductors are currently appealing. The first series is based on existing dielectric PIC platforms (e.g. Si, Ge, III–V semiconductors) that reach a high maturity in fabrication and CMOS compatibility. Owing to the functional versatility, III–V semiconductors and their heterostructures hint at all-semiconductor plasmonic PICs fabricated via a single epitaxial growth process. Fig. 17b depicts an InAs-heterostructure-based plasmonic waveguide [168]. The top heterostructure comprises lattice-matched GaSb-InAs with a "broken-gap" band structure, while the bottom heterostructure consists of a lattice-matched



Fig. 18. Semiconductor-based plasmonic modulators. (a) ITO-based plasmonic Mach-Zehnder interferometer (MZI) modulator. Reproduced with permission [321]. Copyright 2021, Springer Nature. (b) Electric field distribution in the ON and OFF operational states in the ITO-based plasmonic MZI modulator. Inset: corresponding mode profiles. Reproduced with permission [321]. Copyright 2021, Springer Nature. (c) Transmission spectra across the C-band telecommunication wavelengths in the ITO-based plasmonic MZI modulator. Reproduced with permission [321]. Copyright 2021, Springer Nature. (d) Sketch of an SPP diode composed of an $In_{0.53}Ga_{0.47}As$ p-n junction. Reproduced with permission [322]. Copyright 2020, De Gruyter. (e) The local electromagnetic field distribution across the modulator with SPPs excited at the p-n junction interface by TM-mode light at 11.4 µm. Reproduced with permission [322]. Copyright 2020, De Gruyter. (f) Experimental (solid lines) and simulated (dashed) reflectivity spectra of the $In_{0.53}Ga_{0.47}As$ grating device under the TM and transverse-electric (TE) polarized modes. Reproduced with permission [322]. Copyright 2020, De Gruyter.

AlSb-InAs-AlSb quantum well. Upon numerical simulations (Fig. 17c), the *n*-InAs/p-GaSb interface resides and travels SPPs. This multiple-layer system sustains an SPP propagation of several hundred µm at 3.3 µm, assisted by the amplifier. The same hetero-structure, as simulated, could also be made into active plasmonic devices such as an SPP source, a detector, or an amplifier. This all-semiconductor plasmonic PIC implies remarkable device reliability, process simplicity and circuit compactness.

The other class of plasmonic semiconductors for PICs exhibits unique properties viable for specific active devices, for instance, Purcell enhancement for accelerated spontaneous emission, ENZ behavior for high refractive index modulation and efficient hotcarrier transfer for enhanced photodetection. This category of semiconductors encompasses VO₂, TiN, ITO, WO_{3-x}, Cu_{2-x}Se, and black phosphorus, paving the way for all-optical logic gates, plasmonic switches, and reconfigurable plasmonic circuits [70,117,168,170]. The emerging PCMs, Sb₂S₃ and Sb₂Se₃ exhibit enormous refractive-index contrasts ($\Delta n = 0.6-0.77$) between the reversible phases with a stable switching endurance of >4000 cycles. They offer a wealth of possibilities in non-volatile, ultralow-loss programmable PICs [228,229].

5.1.1. Plasmonic waveguides

A diversity of waveguide geometries has been proposed to enable routing plasmon polaritons over a long propagation distance. The fundamental plasmonic mode is a radially polarized TM mode owing to the nature of SPPs [16]. Fig. 17d presents a hybrid photonic–plasmonic waveguide comprising the plasmonic TiN strip epitaxially grown on a sapphire substrate (Fig. 17e) capped with a SiN_x cladding [295]. As revealed by the mode profile in Fig. 17f, the TiN waveguide sustains a hybrid photonic–plasmonic mode, where the long-range polariton propagation is attainable by designing the cladding thickness for the matching of the superstrate and substrate index. As a result, this hybrid waveguide reaches the plasmon propagation length of up to 7.2 mm and a propagation loss of 0.6 dB/mm at 1550 nm. It demonstrates a diminished propagation loss and better mode confinement than the metal plasmonic waveguides of similar configurations. Fig. 17g shows a GaN/GaAs slot waveguide, in which GaAs behave as the dielectric and plasmonic under 800 nm and 1550 nm irradiation, respectively [171]. The GaAs plasmonic mode shrinks substantially compared to the dielectric mode. The VO₂ film realizes a rewritable waveguide at arbitrary positions without material damage, implemented by the monoclinic dielectric-metallic phase alteration via the scanning probe-based technique [117].

III–V semiconductors comprise a diversity of plasmonic waveguides via theoretical simulation. Owing to its small electron effective mass, InAs has been an intriguing plasmon hosting semiconductor of high plasmon frequency and low loss [168,254,307]. Besides, other ever-proposed semiconductor plasmonic waveguides include highly doped *n*-type Ge/Ge, highly doped *n*-GeSn/GeSn hetero-structures [308], highly doped *n*-type InAs slot waveguides [169], doped InGaAs spheres/MgF₂/InGaAs waveguides [170], and GaN/



Fig. 19. Semiconductor-plasmon-enhanced photodetectors. (a) A photodetector based on MAPbI₃/Cs_xWO₃/NaYF₄/CS1, in which the plasmonic Cs_xWO₃ layer enhanced the device performance. Reproduced with permission [158]. Copyright 2019, Elsevier. (b) Simulated electric field distribution of the Cs_xWO₃ film under 980 nm illumination. Reproduced with permission [158]. Copyright 2019, Elsevier. (c) Responsivity and external quantum efficiency (EQE) of the pristine Cs_xWO₃ and plasmon-enhanced MAPbI₃/Cs_xWO₃/NaYF₄/CS1-based photodetectors. Reproduced with permission [158]. Copyright 2019, Elsevier. (d) Schematic illustration of photodetectors based on the hybrid structure of ITO nanoparticles/single-layer graphene/Ge nanorod arrays. Reproduced with permission [107]. Copyright 2016, Wiley-VCH. (e) Simulated electric field distribution at the interfaces among ITO nanoparticles, graphene and a Ge nanorod. Reproduced with permission [107]. Copyright 2016, Wiley-VCH. (f) Self-powered photoresponse under 1550 nm illumination with and without the enhancement of plasmonic ITO nanoparticles. Reproduced with permission [107]. Copyright 2016, Wiley-VCH.

GaAs-based slot waveguides [171]. Aside from waveguides, other passive components can also be made of plasmonic semiconductors, such as a doped-Si-based plasmonic resonator [309], a Si-doped InAsSb plasmonic resonator [50], and a graphene THz band-stop filter [183].

5.1.2. Plasmonic light sources

In PICs, especially in Si photonics, light sources are mostly hetero-integrated onto the photonic circuit, as Si itself does not provide efficient light-emitting. The lasers or light-emitting diodes (LEDs) are separately manufactured and then incorporated to the passive platform via wafer bonding or transfer printing. Alternatively, the emitting light from free spaces can couple to the waveguide via butt coupling or a grating coupler [310]. A plasmonic light source enables the device miniaturization, ultrafast exciton dynamics and diminished losses [311].

Exploring subwavelength plasmonic nanolasers (spasers) has been a heated yet highly debated topic. Fig. 17h sketches the working principle of a spaser [312,313]. Under electrical pumping, population inversion first occurs in the gain medium, generating energetic excitons (indicated by the black and green arrows). The excitons then transfer their energy to the plasmonic material, exciting SPPs. These SPPs stimulate the excitation of more SPPs via exciton-plasmon mode coupling, eventually causing an avalanche of SPP generation (red arrows). Therefore, a spaser is the coherent oscillation of confined SPPs. A spaser thus shrinks the device dimension and accelerates laser emission. Nevertheless, there has been debate about whether the spaser is a feasible and efficient light source, mainly due to its high lasing threshold and strong damping of free-carrier oscillation [314,315]. Khurgin *et al.* argued that the loss compensation in a spaser is constrained by the Purcell enhancement of the spontaneous emission, which results in undesirably high pumping densities exceeding 1 MA \cdot cm⁻² [314]. The Purcell effect is expressed as:

$$F_{purcell} = \frac{3}{4\pi^2} \left(\frac{\lambda}{n}\right)^3 \frac{Q}{V_m},\tag{21}$$

where $F_{purcell}$, n, Q and V_m denote the Purcell factor, refractive index, cavity quality factor and mode volume, respectively [61,303]. A scaling law was proposed as a remedy, viable for the spaser with its cavity size close to or surpassing the diffraction limit. Under such circumstances, a spaser outperforms a photonic laser in terms of the device dimension, emission lifetime and lasing threshold [316]. Despite the high internal loss, the plasmonic material coated outside the dielectric cavity laser can mitigate the far-field radiative loss [311]. Fig. 17c shows the simulated power flux profile of an all-semiconductor plasmonic laser. In this spaser prototype, plasmons are launched and bounded at the GaSb/InAs heterogeneous interface, while the AlSb/InAs/AlSb quantum well is the gain medium [168]. This all-semiconductor spaser features a lower optical loss, improved field confinement, and a broader tuning range for resonant interactions.

Semiconductor plasmonic emitters also emerge as feasible light sources, where the plasmonic light-emitting diode (LED) could reach an energy conversion efficiency equivalent to a laser [314]. The plasmonic LED showcases accelerated radiative dynamics and enhanced spontaneous emission. The emission acceleration mainly derives from the Purcell effect [60,63,314]. When depositing a plasmonic TiN nanoarray film on light-emitting CdSe/CdS/ZnS/CdS core–shell nanoplatelets, the radiative decay rate (0.27 ns⁻¹) at 650 nm was nearly twice that for the identical emitters coated on a glass substrate [55]. Aside from accelerated radiative transition rate, semiconductor plasmonic LEDs also exhibit the augmented intensity of spontaneous emission due to the plasmon-exciton coupling. These two effects, along with plasmonic thermalization, govern the wavelength-selective PL enhancement. In the lanthanide-doped upconverting nanoparticles (UCNPs), incorporating plasmonic WO_{3-x} nanocrystals leads to a >500-fold improvement in PL intensity [65]. A similar scenario is also observed in the heterostructures of PbS QDs and plasmonic Cu_{2-x}Se nanocrystals [64]. Strugo *et al.* numerically studied the plasmon-assisted Cooper-pair-based two-photon emission in a superconducting Nb layer [317]. With an SPP mode traveling along the interface between the highly doped *n*-type InGaAs and Nb layers, the superconductor-semiconductor waveguiding system witnesses a 45-fold enhancement in mode confinement and the two-photon gain elevated by 3 orders of magnitude, implying a high potential in two-photon lasing.

5.1.3. Plasmonic electro-optic modulators

Electro-optic modulators (EOMs) are an indispensable component in PICs, which encode signals from the electrical into the optical domain [144,301,318]. When subject to an altering electric field, an EOM changes its refractive index (electrorefraction) or the absorption coefficient (electroabsorption) in accordance, thus, producing optical signals [319]. Electrorefraction is driven dominantly by the plasma dispersion effect, or the Pockels and Kerr effects. The plasma dispersion effect imposes excess carrier injection [24,39,169], while the Pockels and Kerr effects rearrange the microscopic charge distribution via reorienting the internal dipoles in a molecule or a microstructure [140,144]. Electroabsorption relies on the change in the optical absorption coefficient for signal modulation. Electroabsorption modulation is present in bulk semiconductors (denoted as the Franz-Keldysh effect) and quantum wells (known as the quantum-confined Stark effect) [144]. Most plasmonic EOMs rely on the electrorefraction mechanisms to offer ultrafast, compact, and power-efficient modulation [320]. Most plasmonic EOMs in PICs are driven by the plasma dispersion effect, in which the variation in the free-carrier concentration dictates the refractive index changes [319]. The plasmonic mode endures appreciable mode confinement, effectively promoting light-matter interaction, power efficiency, and even nonlinear polarization [5,144,319]. Haffner *et al.* reported a Si-waveguide-integrated all-plasmonic Mach-Zehnder modulator, reaching an exceedingly good performance, including an ultrashort device length of 10 μ m, a 70 GHz electrical bandwidth, a 72Gbit S⁻¹ operation speed, and an ultralow 25 fJ bit⁻¹ energy consumption [320]. Besides, a plasmonic metasurface comprising staggered netlike two-dimensional electron gas nanostructures could endure the THz wave modulation up to 3 GHz, deriving from the collective-individual state conversion [266].

Degenerate semiconductors possess inherent advantages for plasmonic EOMs due to their unique ENZ behaviour [24,128]. As plotted in Fig. 13b, the ENZ property relies on the electrical modification of the semiconductor permittivity to realize electro-optical modulation. Under the gate bias, the ENZ point of a semiconductor film shifts, switching between the presence or absence of the carrier accumulation layer. Thus, the film shows a reversible metallic-dielectric response at the same incidence wavelength, functioning as the two modulation states [239]. Nowadays, plasmonic EOMs have harnessed many plasmonic semiconductors, such as ITO, Al:ZnO, TiN, In_2O_3 and III–V semiconductors [5,140,144,321]. Amin *et al.* developed an on-chip plasmonic phase shifter consisting of a Si Mach-Zehnder interferometer and the plasmonic ITO coated on one arm, as sketched in Fig. 18a [321]. The signal ON/OFF modulation is realized by switching the ENZ behavior in ITO under gating, as manifested by the simulated electric field distribution in Fig. 18b. As shown in Fig. 18c, the modulator possesses an operation band covering the telecommunication C-band and a GHz-level bandwidth. Vinnakota *et al.* developed a plasmonic modulator based on an InGaAs *p*-n⁺⁺ junction, with the device configuration depicted in Fig. 18d [322]. The simulated field profile in Fig. 18e verifies the SPP excitation at the *p*-n interface. The FTIR spectra in Fig. 18f indicate that the reflectivity change is highly susceptible to light polarization and the applied voltage, which determines the modulation behaviour in the MIR range of 6–14 µm. The device showcases a high modulation depth, a mitigated insertion loss, and a data modulation rate of 1 Gbit/s.

5.1.4. Plasmon-enhanced photodetectors

A plasmonic photodetector couples a plasmonic mode to the photodetector channel. The plasmon integration comprehensively improves the photodetection capability, shrinks the device footprint, increases energy efficiency, and enables remote sensing [18,323]. Unlike conventional photodetectors detecting only light intensity, plasmonic counterparts collect a wealth of information from incident photons, such as intensity, wavelength, and polarization [8,15]. Plasmonic photodetectors mainly profit from two plasmonic effects: near-field enhancement and hot-carrier injection. To date, a variety of device architectures have been demonstrated: quantum well photodetectors [57,324], Schottky barrier photodetectors [325], *p-i-n* photodiodes [90], photoconductors [326], and ring-resonator-integrated photodetectors [182,219,255]. Generally, the plasmon coupling in photodetectors can be implemented in two ways. One is to use the plasmonic semiconductor itself as the light absorber, while the other is to incorporate plasmonic nanostructures onto the photodetector channel.

Plasmonic 2D materials are widely explore for photodetectors, especially in the range. a In the former category, 2D-material-based THz photodetectors are representative devices. These graphene or topological insulators THz detectors in a field-effect transistor configuration are governed by the plasma wave excited in the channel and work in the overdamped plasma region [187,223]. They are



Fig. 20. Water treatment and photocatalysis assisted by plasmonic semiconductors. (a) Steady-state thermal image of a $TiO_{1.67}$ layer. Reproduced with permission [10]. Copyright 2016, Royal Society of Chemistry. (b) Time-resolved temperature change of Si (black curve), Au on Si (blue curve) and a $TiO_{1.67}$ layer on Si (red curve) Reproduced with permission [10]. Copyright 2016, Royal Society of Chemistry. (c) Ion concentrations in seawater before and after desalination by MOO_{3-x} nanoflowers. The corresponding world health organization (WHO) standards are also listed. Reproduced with permission [111]. Copyright 2019, Elsevier. (d) UV–visible spectra and photos (inset) of methylene blue (MB) before and after dye adsorption by charged MOO_{3-x} . Reproduced with permission [111]. Copyright 2019, Elsevier. (e) UV–visible–NIR absorption spectra and wavelength-dependent apparent quantum yield (AQY) photocatalytic CO production on Bi_2O_{3-x} . Reproduced with permission [7]. Copyright 2021, Wiley-VCH. (f) Mars-van Krevelen pathway of photocatalytic reduction of CO_2 on Bi_2O_{3-x} . Reproduced with permission [7]. Copyright 2021, Wiley-VCH. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

tantalizing for medical diagnostics, night-vision, gas sensing, wireless communications, homeland security, *etc.* Besides, plasmonic semiconductors could act simultaneously as the channel material and the hot-carrier source in photodetectors. Hussain *et al.* explored a self-powered photodetector based on plasmonic TiN nanocomposites [9]. Hot electron-hole pairs were excited under light radiation at 365–645 nm, which fell into the LSP spectral regime of TiN. TiN collects the excited hot electrons, while the surrounding nanocomposites collect hot holes. Under weak irradiation of 3.5 mW/cm^2 , this TiN photodetector renders a detectivity (*D**) of up to 1.92×10^{11} Jones.

The local optical confinement induced by external plasmon sources facilitates photocarrier generation in the plasmonic photodetector when the incident photon energy exceeds the bandgap of the light absorber [327]. The common plasmon hosts include TiN [99], Al:ZnO [325], GaAs [324], InAs [90], TiS₂ [90], and graphene [326]. Fig. 19a depicts a plasmon-enhanced multilayer perovskite MAPbI₃ photodetectors [158]. A plasmonic Cs_xWO₃ nanocrystal film was cast on top of the MAPbI₃ layer. After depositing a coating of NaYF₄ as a spacer, a layer of lanthanide-doped upconversion nanoparticles (named m-CS1) was assembled on top of the stack. m-CS1 contains core–shell upconversion nanoparticles of NaYF₄:Yb³⁺, Er³⁺@NaYF₄:Yb³⁺, and Tm³⁺. Under light exposure at 980 nm, the



Fig. 21. Smart windows and solar cells mediated by plasmonic semiconductors. (a) Working principles of electrochromic and thermochromic windows. Reproduced with permission [233]. Copyright 2017, Wiley-VCH. (b) Z-contrast STEM image of the ITO-in-NbO_x film. Reproduced with permission [284]. Copyright 2013, Springer Nature. (c) Transmission spectra of charged ITO-in-NbO_x film under applied electrochemical voltage of 1.5 to 4 V. Inset: photo of the ITO-in-NbO_x film on a glass substrate. Reproduced with permission [284]. Copyright 2013, Springer Nature. (d) Transmission spectra of multilayer W-doped VO₂ film showing an active switching of LSPR behaviour in 20–100 °C. Reproduced with permission [232]. Copyright 2021, Royal Society of Chemistry. (e) Simulated absorption maps in a Si solar cell with an Au or TiN nanoparticle on it. Reproduced with permission [253]. Copyright 2017, Elsevier. (f) Plot of wavelength-dependent optical carrier generation rate (G_{opt}) of ZrN/SiO₂-decorated perovskite solar cells. Reproduced with permission [354]. Copyright 2020, Springer Nature. (g) Mechanisms in a thermophotovoltaic system. Reproduced with permission [98]. Copyright 2015, Elsevier.

intensity of upconversion luminescence in the m-CS1 nanostructures augments by near-3000-fold after coupling with the plasmonic mode on the Cs_xWO_3 film. The MAPbI₃ film then absorbs the light coming from the enhanced upconversion luminescence, leading to an outstanding photodetection capability, namely, a responsivity (R) performance of 0.33 A/W, external quantum efficiency (EQE) of 42.92 %, a *D** of 4.5 × 10¹⁰ Jones and a response time of 180 ms. As verified by the simulated electric field in Fig. 19b, the device amelioration originated from the synergy of Cs_xWO_3 plasmon excitation and m-CS1 upconversion luminescence.

Hot carrier injection is another attractive mechanism in plasmonic photodetectors, which has no constraint on the bandgap of the light-active (channel) material. Hot carriers contribute to the photocurrent when the photon energy surpasses the barrier height at the hetero-interface between the channel material and the plasmonic semiconductor. Hence, this mechanism is beneficial under the conditions of (i) insufficient absorption or (ii) photon energy well below the channel band edge [91]. Yu *et al.* observed a fast sub-bandgap photoresponse in a WO_{2.9}-graphene photodetector under 633 and 1550 nm exposure [89]. The accelerated photoresponse is closely associated with the ultrafast (<150 fs) hot-carrier transfer from WO_{2.9} to graphene, which overwhelms the electron trapping and carrier recombination in WO_{2.9} arrays. Hot carrier injection is also viable in 0D-1D nano-systems. Fig. 19d depicts a plasmon-enhanced Ge photodetector consisting of Ge nanoneedle arrays capped with single-layer graphene and plasmonic ITO nanoparticles [107]. The simulation results in Fig. 19e substantiate the excitation of hot electrons on ITO nanoparticles and the strong light confinement in the Ge nanoneedles. Hence, the plasmonic photodetector exhibits a strongly enhanced self-powered photoresponse, as demonstrated in Fig. 19f.

5.2. Solar energy utilization

Plasmonic semiconductors provide possible remedies for the energy crisis and environmental pollution. Aside from an ultrabroad plasmonic band covering the solar spectrum, there are other prerequisites for plasmonic semiconductors in green-energy applications. For instance, an extreme surface area is preferred in semiconductor nanostructures acting as plasmonic catalysts. The high surface area promotes catalysis-adsorbate interactions, carrier-transfer efficiency, and stability during photocatalytic reactions [10,82,297]. Similar demands of material properties are raised in solar-driven water treatments for the distillation, purification, and desalination of water. Smart windows leverage semiconductors such as ITO and VO₂ with a strong electrochromic and thermochromic response. Next-generation thermophotovoltaics favors semiconductors with strong thermal durability, such as refractory nitrides.

5.2.1. Plasmon-assisted water treatment

Solar energy harvesting has provoked considerable interests for steam generation in water treatment, water splitting, wastewater purification, and seawater desalination and distillation [8,10,17,111,328]. Plasmonic semiconductors in these processes increase optical absorption and solar energy conversion efficiency across the entire solar radiation spectrum. The absorbed power P_{abs} is quantified as:

$$P_{abs} = \frac{1}{2}\omega \varepsilon_2(\omega) |E|^2, \tag{22}$$

where |E| is the amplitude of the electric field [166]. Therefore, the near-field enhancement increases solar absorption. Furthermore, the nonradiative relaxation of photoexcited hot carriers leads to photothermal conversion.

In practice, steams are generated by focusing sunlight onto a fluid dispersed with plasmonic nanoparticles. Yan *et al.* developed a plasmonic light absorber and evaporator based on self-doped $TiO_{2,x}$ nanoparticles [10]. Fig. 20a reveals a rapid temperature ramp-up from 30 to 80 °C in the $TiO_{1.67}$ layer within 200 s of light exposure, with over 90 % absorbance in the solar spectral range. The heating efficiency of the $TiO_{1.67}$ layer was prominently higher than that of the counterparts of bare Si and an Au layer, as demonstrated in Fig. 20b. Huang *et al.* reported on self-doped $MOO_{3,x}$ (0 < x < 1) nanostructures for seawater desalination and wastewater purification [111]. These nanostructures feature strong LSPRs and a near-perfect absorptivity across the solar spectrum, arising from their high vacancy density and nanoflower-like structures. The desalination (WHO) standard, as shown in Fig. 20c. These nanostructures allow excellent photodegradation of methylene blue, as shown in Fig. 20d. Thus, plasmonic semiconductors possess an excellent wastewater purification capability, including the potential for recyclability with minimal temperature modification in the surrounding medium.

5.2.2. Plasmon-mediated photocatalysis

Photocatalysis provides a pathway for redox reactions with lower energy barriers and higher efficiency upon solar irradiation [329–332]. It is widely explored for CO_2 reduction, H_2O splitting, organic transformation, and contaminants degradation [172,333–335]. Plasmonic photocatalysts congruously enhance the catalytic activity, reaction rate, and responsive range [78,242]. It relies mainly on (i) plasmon-induced optical absorption enhancement across a broad spectral range [82,242]. (ii) Energetic hot carriers that effectively regulate the charge transfer pathways and trigger surface functionality [8,78,113]. (iii) An increase of the catalytic efficiency by plasmonic thermalization [108]. The reaction rate and quantum efficiency in plasmonic photocatalytic reactions are proportional to the photon flux and temperature [7]. This peculiar behavior benefits reaction controllability and tunability for industrial implementation.

Plasmonic photocatalysis is attainable in either single-phase nanostructures or semiconductor hybrids. The single-phase plasmonic photocatalysis should feature both plasmonic and catalytic functioning [8,260]. A nearly 100 % CO₂-to-CO selectivity was obtained in the plasmonic photocatalyst Bi₂O_{3-x} [7]. Fig. 20e displays the Bi₂O_{3-x} absorption spectrum covering the UV–visible–NIR spectral range

with an LSPR band in 600–1400 nm. As a result, the quantum yield at 940 nm was 4 times higher than that at 450 nm, enhanced by hot carrier transfer. The higher efficiency for CO₂ reduction was governed by the massive oxygen vacancies in Bi_2O_{3-x} , following a Marsvan Krevelen pathway. CO₂ and H₂ adsorbed on Bi_2O_{3-x} generate free COO⁻ groups and protons as sketched in Fig. 20f, steps 1–3. Then, the COO⁻ groups are converted into CO; and simultaneously, the consumed oxygen vacancies are regenerated, completing the entire catalytic cycle in steps 4 and 5. Plasmonic 2D TMOs, namely, MoO_{3-x} and WO_{3-x}, are also appealing for photocatalysis. They feature the favorable properties of the extreme surface area, a stoichiometry-dependent bandgap, and high stability during photocatalytic reactions [87,108,336].

Plasmonic semiconductor heterostructures and composites support even higher photocatalytic activity. For instance, $MoS_2@TiO_2$ nanocavity arrays form a co-photocatalyst system for H₂ evolution [110]. These nanostructures exhibit a UV–visible-NIR catalytic activity and a high H₂ evolution rate of 181 mmol·h⁻¹·cm⁻². The origins of the excellent catalytic activity encompass the MoS_2 LSPRs in the 400–600 nm region, UV absorption of TiO₂, and NIR absorption of MoS_2 . The 2D MoS_2 nanostructures embedded in TiO₂ cavities facilitate the interaction between photocatalysts and reactants. Besides, the heterostructure provides more carrier transfer routes while



Fig. 22. Vibrational spectroscopy enhanced by plasmonic semiconductors. (a) Mechanistic illustration of surface-enhanced Raman scattering (SERS). Reproduced with permission [49]. Copyright 2016, SPRINGER. (b) Raman spectra of R6G with signals enhanced by H_xMoO_3 prepared with different Cu-acid treatment durations. The SERS mappings underneath reveal excellent uniformity with a LOD of 1×10^{-9} mol/L. Reproduced with permission [196]. Copyright 2020, Wiley-VCH. (c) Photoacoustic (PA) images of tumor-bearing mice with and without injection of plasmonic MoO_{3-x} nanobelts under excitation by NIR lasers of different wavelengths. Reproduced with permission [262]. Copyright 2021, Wiley-VCH. (d) Thermal images of a MoO_{3-x} -injected tumor area under laser irradiation (0.75 W cm⁻²) for 0–10 min, reflecting plasmon-induced localized heating. Reproduced with permission [262]. Copyright 2021, Wiley-VCH. (e) Optical-fibre-based gas sensor enhanced by plasmonic 2D WO₃. Reproduced with permission [204]. Copyright 2019, Wiley-VCH. (g) Optical fiber coated with UCNPs and WO_{3-x} for temperature sensing. Reproduced with permission [204]. Copyright 2019, Wiley-VCH. (g) Optical fiber coated with UCNPs and WO_{3-x} for temperature sensing. Reproduced with permission [65]. Copyright 2019, Royal Society of Chemistry.

boosting photocarrier separation. Plasmonic composites, for example, ternary compound $Mo_xW_{1-x}O_{3-y}$, sustain a profound LSPR due to the high density of native vacancies, yielding 100 mol % conversion of ammonia borane under visible light radiation [210]. Plasmonic catalysts of 3D hierarchical structures also foster photocatalysis via enhanced photon harvesting, carrier separation, and conductivity of hot carriers [299].

5.2.3. Plasmonic smart windows and solar cells

A smart window dynamically adjusts the transmittance of solar radiation. It tailors IR transmission in response to environmental temperature changes while maintaining daylight transparency [33,147,206]. Self-regulation of the window transmittance has been governed mainly by electrochromic or thermochromic effects. As shown in Fig. 21a, the electrochromic effect tunes the window transmittance via repetitive electrical charging/discharging. The thermochromic effect relies on the phase transition of PCM semiconductors [233]. A primary downside of the conventional smart coating is poor wavelength selectivity [259]. Plasmonic semiconductors can address this long-existing issue due to their superior optical tunability over the visible–NIR spectral range. These plasmon-mediated smart windows allow dynamic transmittance switching in an active, reversible, and wavelength-selective manner [261].

ITO has been a widely used plasmon host for electrochromic smart windows. García *et al.* discovered a 35 % NIR transmittance change between bleached and coloured states in the ITO coating [127]. To enhance the optical contrast and electrochemical stability of smart windows, plasmonic ITO nanocrystals were covalently linked to amorphous NbO_x glass via ethanedithiol cross-linking ligands, as shown in Fig. 21b [284]. In response to electrochemical charging and discharging over a voltage range of 2.5 V (Fig. 21c), the ITO–in–NbO_x film could actively and reversibly tune the LSPR response, enabling selective and independent blocking of light in the visible or NIR regimes. The ITO smart windows reach a coloration efficiency of $499 \pm 47 \text{ cm}^2 \text{ C}^{-1}$ [288]. Electrochromic smart windows have also been explored in Al:ZnO, FICO, Nb:TiO₂, and WO_{3-x} [103,141,154,247]. Nevertheless, electrochromic windows still suffer from high cost, a complicated structure and the need for an external energy supply. VO₂-based thermochromic windows have drawn much attention for device simplicity and cost-effectiveness [162,167,238]. Via delicate design of the defects, dopants, and nanocrystal sizes, smart windows based on an Mg/W-doped VO₂ coating film allow a record-high tunability of its LSPR energy in 0.66–1.16 V, as present in Fig. 21d [232].

Photovoltaics has become an essential energy source. Plasmonic solar cells strengthen solar light absorption via mechanisms including (i) the sunlight trapping effect, (ii) plasmon-enhanced light absorption and (iii) light guiding by the plasmonic mode [14]. Hence, plasmonic photovoltaics shrinks the semiconductor absorber's necessary volume and improves the device's stability. Plasmonic semiconductors, particularly TiN and ZrN, are appealing for plasmonic photovoltaics. Plasmonic TiN nanoparticles enhanced Si thin film solar cells can achieve similar absorption to their counterparts based on Au nanoparticles, as demonstrated by the numerical study in Fig. 21e [253]. The performance improvement stems from the synergy of light trapping and absorption effects. ZrN/SiO_2 core/shell nanoparticles on perovskite solar cell, where the ZrN LSP mode directs and couples sunlight into the perovskite active layer, giving rise to a remarkable field enhancement at the ZrN/SiO_2 - perovskite interface, as shown in Fig. 21f. It yields an evident increment of optical carrier generation rate (G_{opt}) in the ZrN LSP bands, reaching a theoretical 20 % power conversion efficiency.

Thermophotovoltaics bypasses the issues raised by the direct solar exposure of the active layer in photovoltaics, which deteriorates the energy conversion efficiency and device stability. As sketched in Fig. 21g, the basic working principle relies on an additional absorber and emitter deposited on top of a conventional photovoltaic solar cell [98]. The absorber generates heat in the intermediate layer under solar radiation. The absorber, and other thermal sources, heat the emitter to reradiate light within a selective energy range. Consequently, the thermophotovoltaic solar cell exhibits a higher conversion efficiency and a longer lifetime. TiN echoes all requirements for thermophotovoltaics [98]. Due to its melting temperature of up to 2900 °C, the TiN nanorings withstand the radiation of high-power laser pulses. TiN serves as an absorber with good spectral selectivity induced by LSPR.

5.3. Sensing and biological applications

Sensing and biological applications are the main driving forces to develop plasmonic semiconductor nanostructures. Semiconductors are preferable for sensing applications due to the high environmental susceptibility and unity-order index alteration [218]. Plasmonic semiconductor sensors allow phase interrogation, in addition to the common sensing strategies to track the intensity and wavelength variation [337]. Besides, plasmonic sensors based on semiconductor nanostructures, especially nanocrystals and 2D materials, allow better adsorbate-plasmon interaction, instantaneous biochemical-process monitoring, device scaling, and *in vitro* diagnostic testing [106,338]. Plasmonic semiconductors are favored for biosensing and chemical sensing when their plasmonic bands spectrally overlap with the biological transparency window and MIR molecular fingerprint window, respectively. Notably, the biological transparency window allows deep light penetration into living tissues with negligible scattering and absorption by tissues and biological fluids [104–106,156,296]. On the other hand, bioimaging and hyperthermia therapies usually count on photothermal effects in plasmonic units. Semiconductors exert inherent advantages in aforementioned applications, especially those with plasmonic thermalization, high biostability, low cytotoxicity, and non-photobleaching nature. Thus, semiconductors including 2D TMOs, ITO, TiN and Cu chalcogenides have been widely explored for plasmonic sensors and bio applications.

5.3.1. Biosensing

Plasmonic semiconductors possess innate advantages for biosensing at physiological concentrations or even at the single-molecule level. The merits mainly lie in their sensitivity to environmental refractive index changes, biostability, and non-photobleaching nature. Therefore, they can overcome the bottlenecks from which conventional bioagents have long suffered: vascular permeation, renal toxicity, and short circulation times [14,339]. Their ultrafast plasmon dynamics ensure a rapid response for monitoring biochemical processes. Some semiconductors, such as MoO_{3-x} and ReO_{3-x} exhibit a biodegradable and self-excretion property. It remains stable in hypoxic and acidic tumor environments while degradable in common physiological surroundings [122,262]. Depending on the detection species, biosensors are categorized into DNA-, immuno-, cell-, antigen-, and molecular imprinting-based sensors [340].

5.3.1.1. Enhanced spectroscopy. Popular enhanced spectroscopy techniques include SERS, surface-enhanced IR absorption spectroscopy (SEIRAS), and surface-enhanced fluorescence (SEF). We focus our discussion on SERS, which relies on plasmonic semiconductor nanostructures to amplify the signals in Raman spectroscopy [194]. Raman spectroscopy allows fast, nondestructive, and noninvasive recognition of analyte "fingerprints". Nevertheless, it suffers from weak signal intensities [1,341–344]. As depicted in Fig. 22a, a SERS substrate is covered with plasmonic nanostructures, significantly enhancing the near-field at the plasmon frequency. Hence, the loading of analytes onto a SERS substrate, even at extremely low concentrations and under complex environmental conditions, leads to an evident field perturbation and Raman signal amplification [113]. The origins of SERS rely on two fundamental mechanisms, electromagnetic field (EM) enhancement, and charge transfer (CT) enhancement [15,196,245,343]. The EM process is governed by the plasmon-induced near-field enhancement around the hotspots. The CT mechanism counts on the vibronic coupling between target molecules and the SERS substrate. During the CT process, the hot-carrier injection and defect states on the SERS substrate facilitate the charge transfer and analytes' chemisorption [81,120,343]. To quantify the SERS effect, two figures of merit are generally used: the enhancement factor (EF) and the limit of detection (LOD). The EF reflects a SERS substrate's ability to amplify Raman signals, defined as:

$$G = \frac{I_{surf}}{N_{surf}} \times \frac{N_{Raman}}{I_{Raman}},$$
(23)

where I_{Raman} and I_{surf} are the intensities of regular Raman and SERS signals, respectively. N_{Raman} and N_{surf} are the numbers of molecules probed via normal Raman spectroscopy and SERS, respectively. The EF is proportional to the fourth power of the near-field enhancement [196]. The LOD denotes the lowest detectable analyte concentration in a SERS system [116].

Plasmonic semiconductor nanostructures can reach high detection selectivity with mitigated background interference in SERS [338]. They open up new opportunities in biomolecular detection, medical diagnostics, immunoassays, and nanotherapeutics [105,345]. Among all semiconductor SERS substrates, 2D materials have aroused growing interest, as their extreme surface-to-volume ratio and atomic thickness allow intimate interaction between 2D materials and the analyte [212]. H_xMoO_3 has shown the best SERS performance among all plasmonic semiconductors with an EF of 1.1×10^7 and a LOD of 1×10^{-9} mol/L [196]. The Raman spectra in Fig. 22b reveal the LODs of different H_xMoO_3 SERS substrates treated by Cu-acid and Zn-acid to induce a higher density of free electrons. The Raman mappings illustrate the µm-scale signal uniformity of different vibrational modes (Raman peaks) at the LOD. SERS biosensors have also been exploited in doped $MoO_{3\cdot x}$ nanocrystals [176], MoO_2 nanospheres assembled on graphene oxide [116], assembled $W_{18}O_{49}$ bundles [346,347], group IVB, VB and VIB TMOS [95], h-BN, 2D titanium carbide or nitride (MXenes), black phosphorus [42], and amongst others. Despite the rapid progress, plasmonic semiconductors remain much inferior to metal-based SERS substrates in terms of EF [343]. The biggest enemy against its application is the aggregation of colloidal semiconductor nanoparticles when serving as detection probes in solution [15]. Besides, organic contaminants attach to the SERS substrate severely degrade the semiconductor plasmonic biosensors, deteriorating their sensitivity, reproducibility, and accuracy [260,348].

5.3.1.2. Other sensing scenarios. Plasmonic semiconductors are also widely explored for the film- or fiber-based biosensors. Plasmonic TiN is a promising material candidate owing to its high hardness, low resistivity, corrosion resistance, and widely tunable visible-NIR plasmonic response [160,165]. Qiu *et al.* demonstrated TiN-film-based biotin-functionalized SPR biosensors [165]. The TiN biosensors exhibit a differential phase sensitivity of 1.932×10^{-7} RIU to refractive-index changes and label-free biotin detection down to $0.22 \,\mu g/ml$ (0.90 μ M), comparable to the Au counterparts. The appreciably high TiN-biotin affinity is attributed to the stacking formation of Ti-N and Ti-O bonds and the high adsorption energy of -1.85 eV. The surface passivation of plasmonic biosensors based on TiN nano-structures facilitates physiological stability and blood retention, which is usually realized by the native oxide or ligand exchanged by PEG (PEGylation) [106,160,165]. Khalil *et al.* have incorporated TiN with photonic crystal fibers to attain biosensing capability under linearly-polarized light modes. The sensor offers better controllable dispersion and design flexibility, reaching high refractive index sensitivity of 7700 and 3600 nm/RIU under propagating light of quasi-TE and quasi-TM modes with high linearity, respectively [160].

5.3.2. Bioimaging and photothermal therapy

Bioimaging provides means for in vivo or *in vitro* visualization of biological components, including tissues and biomolecules. It also enables real-time monitoring of biochemical reactions. To date, PA imaging has emerged as an exciting frontier, which probes thermodynamic expansion of the irradiated region of analytes based on the Doppler effect [11,12,14,18,103,104,248,249,349]. 2D $MOO_{3.x}$ and $WO_{3.x}$ nanostructures are promising PA imaging agents, stemming from their high surface-to-volume ratio, biocompatibility, biodegradability, and low toxicity [258,262]. Fig. 22c showcases the PA images of tumor-bearing mice in an aqueous solution with and without plasmonic $MOO_{3.x}$ nanobelts [262]. Under laser radiation in the $MOO_{3.x}$ plasmonic band (700–950 nm), the samples show an evident signal amplification via incorporating $MOO_{3.x}$ nanobelts. Notably, the intensity of PA signals fits linearly to the $MOO_{3.x}$ concentration, implying a good controllability of the PA imaging amplitude.

Plasmonic semiconductors also see high potentials in hyperthermia therapy, including radiotherapy and photothermal therapy (PTT) [11,12,122]. It destroys tumor cells by plasmonic thermalization without harming healthy tissues. Under high-energy radiation,

the plasmonic thermal effect converts light into heat in the target cancerous tissues, causing cell annihilation, deoxyribonucleic acid (DNA) damage, and tumor remission. 2D TMOs and Cu chalcogenides have reached a level of competitiveness for this application. Fig. 22d displays thermal images of tumor-bearing mice injected with plasmonic MOO_{3-x} nanobelts under 1064 nm laser radiation. Upon increased exposure duration, the plasmonic thermal effect leads to gradual ramps of the local temperature for tumor eradication. The PPT agent yields a high extinction coefficient of 18.2 L/g cm^{-1} and a photothermal conversion efficiency of up to 46.9 % [262]. Nevertheless, the practical use of plasmonic semiconductors for hyperthermia therapy still suffers from weak absorption and insufficient extinction in the bio-transparency window. Plasmonic semiconductor–metal heterostructures offer a solution to this issue [11,296]. For example, the synergetic effects in Cu_{2-x} Se–Au heterostructures contribute to an outstanding PPT performance, yielding 80 % photothermal conversion and 45 % improvement of the sensitivity enhancement ratio.

5.3.3. Fiber-optic plasmonic sensors

A fiber sensor detects analytes via evanescent interaction with light propagating along the fiber. A fiber-optic plasmonic sensor is formed by coating a plasmonic layer onto the unclad core of a fiber [204]. It probes the change in local refractive indexes, transmittances, or temperatures. The refractometric effect dominates in the working principle of these sensors. Under this effect, the carrier distribution in plasmonic nanostructures gets disturbed by adsorbate molecules, altering the refractive index of surrounding media. Eventually, the amplitude and phase of light transmitted through the fiber are modified, along with a plasmon frequency shift [189,350,351]. The plasmon resonance and hot-carrier transfer reinforce analyte-plasmon-photon interaction [8,9,18,24], while the plasmonic thermal effect allows a reversible and controllable sensing process [27]. Fiber-optic plasmonic sensors support real-time sensing with excellent sensitivity, accuracy, device compactness, gas selectivity, and mechanical flexibility [18].

Along with classical plasmonic semiconductors [279,352], 2D TMOs have sparked considerable interest because of the better adsorbate-plasmon interaction from extreme surface-to-volume ratio, massive free carriers from ion intercalation, and ultrabroad sensing range [18]. Fig. 22e depicts a NO₂ sensor based on plasmonic WO_{3-x} in which a thin layer of exfoliated WO_{3-x} covers a D-shaped, side-polished, single-mode optical fiber [204]. Due to the paramagnetic nature of NO₂, this fiber sensor demonstrates excellent NO₂ sensing selectivity [264]. The WO_{3-x} SPR band overlaps with the wavelength of the guided light. Surface NO₂ adsorption redistributes free carriers in the WO_{3-x} layer, suppressing the intensity of detected light. Fig. 22f indicates its dynamic and stable sensing in the NO₂-in-N₂ concentration range of 44–704 parts per billion (ppb) at 160 °C. The WO_{3-x} fiber sensor also demonstrates temperature sensing. Using a heterogeneous combination of WO_{3-x} and lanthanide-doped UCNPs (Fig. 22g), the sensor works in the broad range 306–1354 K with a high resolution of 0.17–1.18 K [65]. In addition, plasmonic-MOF nanocomposites further improve the surface functionalities, for instance, a NO₂ sensor based on core–shell H_xMOO₃-Fe MOF structures [298].

6. Conclusions and outlook

Semiconductor plasmonics has developed into a new frontier for nanometer scale light manipulation in the UV to THz wavelength regions offering very high flexibility for tailored optical properties. Classical plasmonic semiconductors are oxides, chalcogenides, nitrides, and III–V semiconductors. Emerging 2D materials and PCMs provide plasmonic systems sustaining (i) strong plasmon resonances with low losses and (ii) unique phenomena such as plasmonic hyperbolicity, plasmonic twistronics, plasmonic spintronics, anisotropic plasmons or nonlinear plasmonics.

Highly doped semiconductors sustain ultra-high flexibility in plasmon dynamics and properties. The plasmon excitation substantially amplifies the near-field, while plasmon Landau damping allows hot carrier injection and plasmonic thermalization. Investigating hot-carrier transfer pathways, either direct or indirect, benefits their utilization in heterogeneous plasmon-adsorber systems. Semiconductor plasmons exhibit high flexibility, which is compositionally, structurally and morphologically tailorable by various *insitu* approaches. Semiconductor hybrids provide more degrees of freedom to regulate plasmonic response. Specifically, metasurfaces support collective plasmonic modes, plasmonic surface lattice resonances, and extended plasmon propagation. Heterostructures can achieve broader spectral ranges, reinforced plasmon interaction, or high surface affinity for intimate plasmon-analyte interaction. The post-synthetic plasmon manipulation makes semiconductors even more unique and versatile, which stems from their sensitivity to the environment and surface coordination. The practical routes include (i) applying the electrochemical, electrostatic and photochemical fields and (ii) ion and ligand exchange.

Plasmonic semiconductors spawn a cascade of applications, mainly taking advantage of their distinctive plasmon dynamics and tunability. Integrated plasmonics primarily relies on semiconductors' potential to sustain a negative real-part permittivity and mitigated loss. Therefore, they confer on-chip passive and active components with high efficiency, miniaturized footprints, and longdistance signal propagation. Plasmonic semiconductors also make use of damping-induced hot carriers and plasmonic thermalization, which encompasses applications in photon detection, water treatment, photocatalysis, thermophotovoltaics, biosensing, imaging, and hyperthermia therapies. In addition, their dynamic and reversible plasmonic response benefits electro-optic modulation, smart windows, self-cleaning catalysts, and recyclable sensors.

Despite the high promise that plasmonic semiconductors hold, their development remains in its infancy. So far, the physical understanding of plasmon dynamics, such as hot-carrier transfer and thermal dissipation pathways, remains elusive for real-world applications. The newly discovered direct transfer pathway is appealing because it accelerates the transfer rate to 20–50 fs (compared to 100 fs–1 ps in indirect transfer) and increases the energy conversion efficiency by more than an order of magnitude. The fundamental studies of plasmon physics in semiconductors call for a direct visualization of plasmons on semiconductors, which demands further advances in imaging techniques [63,78]. Regarding experimental aspects, a better plasmon manipulation capability requires the dynamic control of discrete states in the band structure. The tempting quantum plasmonics motivates scientists to synthesize colloidal

nanocrystals with nanometric precision. The call for new functionalities surges the development in constructing semiconductor metasurfaces and heterostructures with higher accuracy and controllability. The practical use of post-synthetic routes for plasmon engineering, such as hot-carrier-related photochemistry, demands promoting energy conversion efficiency.

Nowadays, plasmonic semiconductors are still facing challenges for competitive applications. Plasmonic integrated circuits are hindered by a relatively slow speed of electro–optic modulation. Thus, exploring plasmonic semiconductors with prominent epsilonnear-zero behaviour, ballistic transfer, and mitigated impurity scattering has become a strong drive. Another well-motivated trend is to explore plasmonics at longer wavelengths benefitting from the plasmon band of semiconductors. For instance, the MIR region confers manageable losses and is promising for spectroscopic sensing and free-space communications [314]. Combining plasmonic modes with phonon modes or Mie resonances opens new gates for ultrafast, ultrasensitive, and broadband plasmonic devices at SWIR–LWIR wavelengths. In conclusion, plasmonic semiconductors have expanded the spectral range and plasmon manipulability. With the booming of related fundamental studies and application prospects, this field establishes its potential for next-generation quantum photonics, programmable plasmonics, green industries, and biosciences.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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