Review

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Plasmonic nanostructures in photodetection, energy conversion and beyond

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Abstract: This review article aims to provide a comprehensive understanding of plasmonic nanostructures and their applications, especially on the integration of plasmonic nanostructures into devices. Over the past decades, plasmonic nanostructures and their applications have been intensively studied because of their outstanding features at the nanoscale. The fundamental characteristics of plasmonic nanostructures, in particular, the electric field enhancement, the generation of hot electrons, and thermoplasmonic effects, play essential roles in most of the practical applications. In general, these three main characteristics of plasmonic nanostructures occur concomitantly when electromagnetic waves interact with plasmonic nanostructures. However, comprehensive review investigating these three main effects of plasmonic nanostructures simultaneously remains elusive. In this article, the fundamental characteristics of plasmonic nanostructures are discussed, especially the interactions between electromagnetic waves and plasmonic nanostructures that lead to the change in near-field electric fields, the conversion of photon energy into hot electrons through plasmon decay, and the photothermal effects at the nanoscale. The applications, challenges faced in these three areas and the future trends are also discussed. This article will provide guidance towards integration of plasmonic nanostructures for functional devices for both academic researchers and engineers in the fields of silicon photonics, photodetection, sensing, and energy harvesting.

1 Introduction

In the past two decades, the concepts and characteristics of plasmonic nanostructures have been intensively investigated and experimentally demonstrated. Typically, there are three main light-material interactions of plasmonic nanostructures involving electric field enhancement, the generation of hot electrons, and thermoplasmonic effects, as illustrated in Figure 1. In general, when the incident light propagates through a plasmonic nanostructure, e.g., gold (Au) nanoparticle (NP), at the designed wavelengths, the free electrons will oscillate collectively on the surface of the plasmonic antennas [1, 2]. In this situation, light will dramatically interact with metallic nanostructures and therefore generally results in the enhancement of electric field around the plasmonic nanostructures [3–5]. In addition, the collective oscillation of free electrons in the plasmonic antenna would be affected significantly by the environments [6]. Such property of plasmonic nanostructures has been widely used to improve the efficiencies of photodetectors and photovoltaics [7–19], and the detectability of sensors [6, 20–22].

Because of the strong light-metallic nanostructure interactions, the incident light will be absorbed by the plasmonic nanostructures to generate plasmon-induced hot electrons [23–32]. Then, the generated hot electrons will make a movement in the metallic nanostructures and might lose energy through inelastic collisions in the metal film. In this situation, if the plasmonic nanostructures contact with a semiconductor to form Schottky barrier and the hot electrons have enough energy to go across the barrier, the hot electrons will inject into the conduction band of the semiconductor to generate current for photodetection well below the band edge of semiconductor [33–45]. Such properties of plasmonic nanostructures could extend the detection capability of semiconductors over their band gaps even though the semiconductors do not absorb the light at the designed wavelengths. In the other situation, if the hot

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Figure 1: Schematic representation of the characteristics of plasmonic nanostructures and their applications. Three main characteristics of plasmonic nanostructures, including the enhancement of electric field around antennas, the generation of hot electrons in a metal film, and thermoplasmonic effects occurring when the incident light propagates through the plasmonic nanostructures. Such attractive properties of plasmonic nanostructures suggested that they have a great potential for use in the fields of photodetection, sensing, and energy harvesting.

electrons depleted their energy in the metal film, the temperature of plasmonic nanostructures will increase significantly within minutes and then gradually saturated with the environment, which is called thermoplasmonic effects of plasmonic nanostructures [46–51]. The thermoplasmonic effects have been widely used in the fields related to energy harvesting [52–56], lithography [57], photothermal therapy [58–64], solar desalination [65, 66], and photodetections [67, 68]. In the following sections, we highlight different experimental strategies of plasmonic-based devices to achieve a high conversion efficiency based on diverse plasmonic nanostructures. Insights on the correlations between structures and properties of plasmonic nanostructures for distinct applications are revealed. Through summarizing the outstanding challenges and future trends in the field, we aim to provide a comprehensive understanding of plasmonic nanostructures and their applications, especially for the integration of plasmonic nanostructures into devices, and to stimulate discussions and ideas accelerating the development of next generation plasmonic devices.

2 Strategy I: Enhancement of electric fields through plasmonic nanostructures

In general, plasmonic nanostructures are attractive because of the properties of their local surface plasmon resonance (LSPR) and nanofocusing [69–73]. The strong interactions between metallic nanostructures and incident

light originate from excitation of the collective oscillations of the electron cloud within the nanostructures. Optical waves can be coupled to the electron oscillations in the form of localized extinction. The LSPR frequencies of metal nanostructures can be tuned readily through variations in their sizes, structures, and morphologies as well in the refractive index of the surrounding medium [74–77]. Therefore, the LSPR features of nanostructures based on metallic nanostructures can be tuned for efficient conversion of incident light and strong confinement and enhancement of the electrical field around the metallic nanostructures. These properties of plasmonic antennas suggested they could be directly used to improve the sensitivity of sensors [77–85], the detection capability of photodetectors, and the efficiencies of photovoltaics [7, 8, 14, 86]. For example, plasmonic nanostructures have been widely used in surface enhanced Raman scattering (SERS) technology [3–5, 77–85, 87–92] since the enhancements of Raman signal intensities are proportional to $|E|^4$. Chou et al. developed an ultra-sensitive SERS substrate based on a hydrophobic rose petal [79]. As displayed in Figure 2A, the surfaces of the rose petals exhibit good hydrophobicities. Therefore, both metallic NPs and analytes could be concentrated and aggregated into a small spot on the rose petal as shown in Figure 2B. Figure 2C displays the scanning electron microscopic (SEM) images of the aggregated Ag NPs with the analytes concentrated on the top surface of the rose petal. They demonstrated that many nanogaps between adjacent Ag NPs can dramatically enhance the electric field and therefore, the Raman signals. As displayed in Figure 2D, the Raman signals of the

Figure 2: (A) Surface wetting property of white, pink, deep pink, and red rose petals. (B) Photographs of the process flow of Ag NPs and analytes on a white rose petal. (C) SEM image of the aggregated Ag NPs with concentrated analytes on surface of rose petal. (D) Measured concentration-dependent Raman spectra of rose petal-based SERS substrates. (E) Reproducibility of the Raman spectra of 10⁻¹² M analyte at 10 different positions on the rose petal-based SERS substrates [79]. Copyright 2015, American Chemical Society. (F) Schematic representation

analytes can be detected even if the concentration of the analytes is only 10^{-15} M. This rose petal-based SERS substrates achieved the limit of detection in the femtomolar regime with high reproducibility (Figure 2E).

Recently, two-dimensional (2D) nanomaterials have attracted intensively research interest because of their outstanding properties and promising applications. Cai et al. proposed a simple approach to manipulate the assembly of nanoparticles to fabricate free-standing 2D quasi-nanosheets (QNS), which perform highly uniform and reproducible Raman scattering over the entire sample area [88]. Figure 2F and G reveals the schematic representation and transmission electron microscopy image, respectively, of the 2D QNS. As shown in Figure 2G, the synthesized 2D QNS are composed of densely packed nanoparticles (NPs). Through their synthesis method, they successfully synthesized 2D palladium (Pd)–platinum (Pt) QNS. They found the synthesized 2D Pd–Pt QNS perform excellent optical characterizations in SERS because the enhancement of electric field around densely packed Pd–Pt NPs. As displayed in Figure 2H, the Pd–Pt QNS perform strong electric field around the Pd–Pt NPs over broadband wavelength regime (365, 532, 633 and 785 nm). The simulated electric field amplitudes ($|E|^2$) of Pd–Pt QNS are at least 1.4 times and 3 times larger than that of Pd NPs and that of Pt NPs, respectively, at each wavelength. Furthermore, they found the areas with large amplitudes of electric field, which called hot spots, exist almost everywhere in the proposed Pt–Pd QNS, because of the densely packed Pd and Pt NPs. Therefore, they observed the synthesized 2D Pd–Pt QNS provide strong and uniform Raman signals in the presence of 2×10^{-6} M Rhodamine B over large area as displayed in Figure 2I and J. Through the enhancement of electric field around metallic nanostructures and nanogaps, many kinds of SERS sensors with high sensitivity and detection capability have been achieved.

In addition, plasmonic nanostructures can be used to increase the harvesting of incident light and enhance the performance of optoelectronic devices, such as solar cells [7–14, 86, 93, 94], sensors and photodetectors [17, 95, 96], and lasers [97]. Conventionally, these metallic nanostructures are placed on or close to the active region of the device, thereby generating a strong electric field within the near field and increasing the photon density of states to modify or enhance the performances of the device. The

interaction of light with nanostructured metals can cause the near-field optical field to increase by several orders of magnitude relative to the incident light. In general, the values of electric field amplitudes ($|E|^2$) are proportional to the input energy flux density. Therefore, the nanostructured metals or their neighboring semiconductor materials can undergo intense absorption of light. Chi et al. proposed and experimentally demonstrated that fabricating periodic hole arrays on the metallic finger electrodes of silicon (Si)-based solar cells can significantly enhance the efficiencies of the devices [86]. Figure 3A and B displays the schematic representation and top-view SEM images, respectively, of the plasmonic Si-based solar cells. They investigated and discussed the optical properties and optoelectronic characteristics of the plasmonic silicon-based solar cells featuring different dimensions of hole and periodicity on the aluminum (Al) finger electrodes. They found that the device featuring periodic hole arrays with the hole of 400 nm and period of 800 nm, which named H04P08 hole array structure, performs excellent optical and optoelectronic performances. As displayed in Figure 3C, the incident light can transmit through the metallic hole array structure into the underlying Si substrate over broadband wavelength regimes, and then be absorbed by Si. Therefore, the external quantum efficiencies of the devices having hole array structures are much higher than those of the devices without plasmonic nanostructures from visible to near-infrared (NIR) regime (Figures 3D). Furthermore, when the devices have the same area of metallic finger electrodes, the devices with hole array structure would perform much better efficiencies than the devices without hole array structure even the metal figure area over total device is only 15% (Figures 3E). Based on these attractive characteristics of hole array structures on metallic electrode, Lin et al. proposed a compact Schottky-based plasmonic color-image sensors featuring high photo-responsibility and low power consumption [96]. They demonstrated that when the Al electrode with hole array structures integrated into the Si-based device, the device would perform not only excellent color splitting ability (Figures 3F) even for the hole array structure with only 33 holes (Figures 3G) but also a good detection capability to several $\text{fW } \mu\text{m}^{-2}$ (Figure 3H). Accordingly, the plasmonic nanostructures have a great potential for direct integration with solar cells, color imaging sensors, and photodetectors to improve their efficiencies, functionalities, and detection capabilities in the low-light environments,

and (G) high-resolution transmission electron microscopy images of 2D QNS. (H) The electric field distributions of the light at the wavelengths of 365, 532, 633, and 785 nm propagating through the 2D Pd–Pt QNS on a glass substrate. (I, J) Measured (I) Raman spectra and (J) intensities of peak signals at 631, 1285, 1365, 1508, and 1648 cm^{-1} of the 2D Pd–Pt QNS at five different positions over the area of 0.25 m^2 [88]. Copyright 2019, American Chemical Society.

Figure 3: (A) Schematic representation and (B) top-view SEM images of plasmonic silicon-based solar cells featuring hole array structures on the metallic finger electrode. (C) The electric field distributions of the light at the wavelengths of 450, 650, and 850 nm propagating through the H04P08 hole array structure on a Si substrate. (D) The external quantum efficiencies of the devices with and without hole array structures. (E) Measured efficiencies of Si-based solar cells with different arrangements of metallic finger electrode [86]. Copyright 2013, Royal Society of

using mature complementary metal–oxidation–semiconductor (CMOS) technology [98–100].

Recently, 2D materials have attracted enormous attention because they feature many promising properties not available in their bulk format and have a great potential to be directly integrated into CMOS devices [101–104]. However, such devices suffer from low photoresponse due to the low absorption by the monolayer 2D materials. Many studies have demonstrated that plasmonic nanostructures can be integrated with 2D materials, such as graphene, MoS₂, and WS₂, to improve their performance [105, 106]. Li et al. proposed and demonstrated a nanoparticle grating based monolayer MoS₂ photodetector [106]. Figure 4A and B displays the schematic representation and SEM image of a MoS₂ device incorporating a nanoparticle-grating pattern. UV photolithography and an annealing step were used to fabricate the nanoparticle grating structure. Then, the fabricated plasmonic nanostructures were transferred onto a monolayer of MoS₂. Compared with Au nanoparticle arrays, the grating structure can increase the extinction over the broad bandwidth due to the improved excitation efficiencies of localized surface plasmons through grating coupling (Figure 4C). Therefore, the photoresponse of the nanoparticle grating/monolayer MoS₂ device is more than 100 times higher than that of the MoS₂ device alone at a wavelength of 532 nm (Figure 4D).

In addition to 2D materials, many studies have demonstrated that the performance of perovskite devices (e. g., photodetector and solar cell) can be significantly improved when plasmonic nanostructures are integrated into the devices [107–114]. Figure 4E and F displays the schematic representation and SEM image of an organic–inorganic hybrid perovskite photodetector on arrays of Au square nanostructures [107]. The underlying Au squares can significantly reduce the reflection, and thus, improve the absorption of the perovskite photodetector over broad bandwidth, in particular close to the band edge of perovskite (Figures 4G), due to the LSPR absorption. Therefore, the external quantum efficiency of the plasmonic perovskite device can be efficiently improved over broad bandwidth and achieved more than 250% enhancement at the wavelength of 800 nm compared with the external quantum efficiency of the device without plasmonic nanostructures (Figures 4H). Accordingly, the performance of the device can be essentially improved when the plasmonic nanostructures are properly integrated with the devices, in particular for the

devices suffering from insufficient absorption (e.g., at the wavelength range close to the band edge of materials).

Many types of plasmonic nanostructures have been developed, including C-shaped nano-apertures [115], nanoslots [116, 117], nanoparticles, and nanoantennas [17, 118], for use in the improvement of photoresponsivity of devices in the infrared (IR) regime. In 2006, Tang et al. proposed the concept of integrating a C-shaped nano-aperture with germanium (Ge)-based photodetector to enhance the photocurrent of the device in the IR regime [115]. Figure 5A and B displays the schematic illustration of the designed C-shaped nano-aperture and the SEM image of the C-shaped nano-aperture fabricated in Au film, respectively. They used focus ion beam (FIB) to fabricate the designed C-shaped nano-aperture structures with feature sizes of less than 100 nm (Figure 5B). The designed C-shaped nano-aperture can enhance the photocurrent of a Ge-based photodetector locally instead of exciting surface plasmon resonances over a long range. As displayed in Figure 5H, the Ge-based device featuring C-shaped nano-aperture reveals polarization-dependent photoresponse in the IR regime that is the direct evidence of an antenna effect. Furthermore, compared with the photodetector having a square nanoaperture with the same area, the Ge-based photodetector featuring C-shaped nano-aperture performs 2–5 times the photocurrent enhancements at a wavelength of 1310 nm [Figure 5I]. The Ge-based photodetector featuring C-aperture performs the maximum photocurrent when the polarization of light is parallel to the two arms of the aperture (*x*-polarization).

In addition, nanoparticles and nanoantennas have been used to confine strong optical electric fields within sub-wavelength volumes for the enhancement of the photoresponses in the IR regime of devices. Open-sleeve dipole-type antenna and plasmonic nanoslot waveguide were designed to construct a planar sub-wavelength metal–semiconductor–metal (MSM) photodetector [116–118]. Figure 5C–E displays the top view and cross-sectional view of schematic representations of the Ge-based photodetector featuring open-sleeve dipole-type antenna. The planar open-sleeve dipole-type antenna is composed of a dipole antenna oriented in the *y* direction and two electrodes in the *x* direction. As displayed in Figure 5J, the open-sleeve dipole antenna could not only enhance the electric fields around the surface of the device but also achieve high polarization selectivity. Therefore, the Ge-based photodetector featuring

open-sleeve dipole-type antenna performed polarization-dependent photoresponse when the devices illuminated with IR light having different polarization states [Figure 5K]. The photocurrent enhancement ratio of the Ge-based device could be as high as approximately 20 in the IR regime. Recently, plasmonic nanostructures

(e. g., nanoslots) have been further integrated with Ge waveguide to achieve high-performance and high-speed photodetection at telecommunication wavelengths [117]. Figure 5F and G displays the schematic representation and SEM images of the plasmonic nanoslot waveguide device. As displayed in the inset I of Figure 5F, light can be

Figure 4: (A) Schematic representation and (B) SEM images of Au nanoparticle grating/MoS₂ hybrid photodetector. (C) Extinction spectra of Au nanoparticles (NP I: diameter/period = 47/110 nm and NP II: diameter/period = 200/600 nm) and Au nanoparticle grating with period of 4 μm. Inset: simulated electric field distribution around NP I. (D) Photocurrents of MoS₂ photodetectors with different plasmonic nanostructures [106]. Copyright 2020, American Chemical Society. (E) Schematic representation and (F) SEM images of perovskite photodetector on Au square arrays. (G) Measured reflection spectra of perovskite films on Si/SiO₂ and plasmonic substrates. (H) Spectral external quantum efficiency of the perovskite devices on Si/SiO₂ and plasmonic substrates [107]. Copyright 2018, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Figure 5: (A) Schematic illustration of the designed C-shaped nano-aperture with featured dimension of less than 100 nm. (B) Top-view SEM image of the C-shaped nano-aperture fabricated in Au film. The scale bar is 500 nm. Copyright 2006, Optical Society of America. (C) Top view and (D, E) cross-sectional views of schematic representations of Ge-based photodetector featuring open-sleeve dipole-type antenna. (D) and (E) are the cross-section view corresponding to line one and line 2, respectively, as indicated in (C). Copyright 2008, Springer Nature. (F) Schematic representation and (G) SEM images of plasmonic nanoslot waveguide photodetector. Inset I in (F): Simulated optical and DC

well confined in the Ge waveguide, and thereafter, be efficiently absorbed by the Ge waveguide. Furthermore, the photogenerated carriers in Ge waveguide can be efficiently separated and then collected through the Au nanoslots under a bias voltage (inset II of Figure 5F). Therefore, such ultracompact plasmonic MSM photodetectors have a great potential for use in on-chip photonic integrated circuits.

In summary, when plasmonic nanostructures are integrated into optoelectronic devices, the use of metallic nanostructures as an optical antenna on a semiconductor material can significantly enhance the photoresponse of a device, mainly from the strong near-field optical intensity around the metallic nanostructures further increasing the absorption of light in the semiconductor materials. However, the dimensions of the plasmonic nanostructures are usually in the range of several tens and hundreds of nanometers. Therefore, the plasmonic nanostructures are generally manufactured by complicated and expensive fabrication processes, e.g., FIB or electron beam lithography (EBL). Accordingly, an essential challenge remains to develop a new plasmonic nanostructures that can be fabricated using high-throughput and low-cost manufacturing processes while dramatically enhance the efficiency of the semiconductor materials.

Furthermore, the generated strong electric field around the plasmonic nanostructures could be used to efficiently improve the detection capability of sensors, e. g., SERS-related devices. The challenges remain in this field are the fabrication of plasmonic sensors, which can feature not only high sensitivity but uniform and reproducible signals, with large scale via a simple method.

2 Strategy II: Generation of hot electrons in the plasmonic-based devices

In addition to the enhancement of near-field electric fields around the active region of optoelectronic devices, the plasmon-induced hot electrons could also be used to improve the efficiencies of optoelectronic devices, especially in the wavelength regime below the band edge of

semiconductor materials [26, 33–35, 37–45]. In 2011, Knight et al. proposed and experimentally demonstrated the concept of using an active antenna for photodetection well below the band edge of the Si-based devices [41]. Generally, the nanoantennas are optical components that can be used to enhance the intensity of electromagnetic field; they could be integrated into photodiodes to enhance the conversion of light to photocurrent for photodetection as discussed in the above section. Their concept was to combine the functions of a nanoantenna and a photodiode within the same structure, which they called an active optical antenna, as shown in Figure 6A and B. They have demonstrated that the hot electrons arising from surface plasmon decay in the active antenna can move across the Schottky barrier and then inject into the conduction band of Si, thereby contributing to the photocurrent directly for the photodetection at optical telecommunication regimes [Figure 6C]. Typically, the bandgap energy of Si is approximately 1.12 eV. This strategy overcomes the native limitations of Si-based devices, which cannot convert the light featuring energy below the band edge of Si to photocurrent. Photocurrent can be generated when the photon energy is only slightly higher than the Schottky barrier height. Furthermore, they proposed and demonstrated that the spectral response of an active antenna-based device can be considered as that of a Schottky diode incorporating with a specific plasmon resonance. For a Schottky diode, the photoresponse depends on the quantum transmission probability (η_i) of the carriers, which can be approximated by the modified Fowler equation,

$$\eta_i \approx C_F \frac{(h\nu - q\phi_b)^2}{h\nu} \quad (1)$$

where C_F is the Fowler emission coefficient, $h\nu$ is the photon energy, and $q\phi_b$ is the Schottky barrier height. Through Eq (1), the number of carriers with sufficient energy to overcome the barrier height and, thereby, contribute to the photocurrent for a Schottky diode in the absence of a specific plasmon resonance can be preliminarily approximated. Then, when the Schottky junction is formed by plasmonic nanostructures, the photoresponsivity (R) of active antenna-based device will show a Fowler response (η_i) modified by the plasmonic absorption (A), which is $R = \eta_i A$.

fields in the devices. Inset II in (F): Energy band diagram of the Au-Ge-Au (MSM) device under a bias voltage [117]. Copyright 2018, American Chemical Society. (H) Measured photocurrent spectra of the Ge-based photodetector featuring C-shaped nano-aperture at distinct polarizations (x-polarized and y-polarized) of incident light. (I) Polarization dependence of the photocurrent of Ge-based photodetector featuring C-shaped nano-aperture at a wavelength of 1310 nm [115]. Copyright 2006, Optical Society of America. (J) Simulated near-field distributions of electric field of the open-sleeve dipole-type antenna 25 nm above the substrate surface. (K) Measured photoresponse spectra of Ge-based photodetector featuring open-sleeve dipole-type antenna for the light with different polarizations (x and y directions) in the IR regime [118]. Copyright 2008, Springer Nature.

Furthermore, the spectral photocurrent and absorbance spectrum of the active optical antennas can be controlled readily by adjusting the dimensions and shapes of the nanoantennas [Figure 6D]. Therefore, as displayed in Figure 6E, the peaks of the spectral responsivity shift to the longer wavelength with the enlargement of the length of nanoantennas. Because of so many attractive properties of active optical antenna, the proposed Si-based photodetectors featuring active optical antennas have a great potential to replace III-V materials and Ge used in current on-chip silicon photonics for receiving signals at telecommunication wavelengths. Therefore, this concept opens a window for the design of on-chip silicon photonics by just using Si materials. Nevertheless, the measured photoresponsivities of this kind of active optical antennas-based devices were only several nA mW^{-1} (lower than 10 nA mW^{-1}) in the IR regime [Figure 6E]. Thus, photoresponse of the Si-based devices featuring active nanoantenna in the IR regime still has a lot of room for improvement.

In order to further improve the photoresponse of the active optical antenna-based devices in the IR regime, Knight et al. proposed a concept of embedding plasmonic nanowires into the semiconductor material to essentially increase the

emission of hot electrons in 2013 [42]. Compared with the planar gold nanowires on Si substrate featuring only one plasmonic decay path [Figure 7A], the embedded gold nanowires within Si substrate possess three plasmonic decay paths [Figure 7B] to support the plasmonic-induced hot electrons effectively transporting through the metal-semiconductor interfaces. They observed that the simulated absorptions of the embedded gold nanowires within Si substrate featuring different embedding depths reveal only small difference [Figure 7C]. However, the photoresponsivity of the active optical antenna-based devices with embedded gold nanowires would be enhanced significantly as the increment of embedding depth of nanowires within the Si substrate, especially for the device with nanowire width less than 100 nm [Figure 7D]. Therefore, the photoresponse of the active optical antenna-based devices might not only be influenced by the absorbance of the plasmonic nanostructures. The geometry of plasmonic nanostructures, the contact area between the metal and the semiconductor material, and the moving distance of hot electrons toward metal-semiconductor junctions should also be taken into consideration for the design and the improvement of photoresponsivity of the plasmonic active optical antenna devices.

Figure 6: (A) Schematic representation of Au nanoantenna on an n-type Si substrate. (B) SEM image of an active optical antenna-based device (imaged at a 65° tilt angle). (C) Energy band diagram of the active optical antenna Schottky-based devices. (D) The measured photocurrent spectra and simulated absorption spectra of the nanoantennas featuring distinct sizes. (E) The measured spectral photoresponsivity of active optical antenna-based devices featuring different dimensions of Au nanoantennas (length: 110, 116, 122, 128, 134, 140, 146, 152, and 158 nm) [41]. Copyright 2011, American Association for the Advancement of Science.

In the same year (2013), Sobhani et al. proposed a concept of integrating Au nanograting [Figure 7E and F] into an active optical antenna device to improve the responsivity of the device for photodetection in the IR regime [45]. The periodic Au nanograting structures could couple the incident light to surface plasmons propagating through the slits of the Au film [Figure 7G]. Therefore, the Au nanograting structures

perform strong absorption at the designed wavelengths. Moreover, the simulated absorption distributions of the active optical antenna device with Au nanograting revealed that the main absorptions of the structured Au layer occur close to the metal–semiconductor interfaces as displayed in Figure 7H. In other words, most of the hot electrons would be generated at the bottom surface of the gold nanograting

Figure 7: SEM images and schematic representations of (A) the planar and (B) the embedded active optical antenna-based devices. (C) Simulated absorption and (D) measured photoresponsivity of the embedded active optical antenna-based devices at a wavelength of 1550 nm for the embedding depth of 5 nm (blue line), 15 nm (green line), and 25 nm (red line). The thickness of gold nanowires is 35 nm for all of the embedded active optical antenna-based devices [42]. Copyright 2013, American Chemical Society. (E) Schematic representation and (F) SEM image of the active optical antenna-based device featuring gold nanograting structure. The scale bar in the SEM image is 1 μm . (G) Propagation of surface plasmon on gold nanograting structures. a, b, and c indicated in (G) is the surface plasmon polaritons oscillating at the top surface, sidewall, and bottom surface of nanograting, respectively. (H) Simulated absorption distributions of Au nanograting on the Si substrate at a wavelength of 1460 nm. (I) Spectral photoresponsivity of the active optical antenna-based device featuring gold nanograting structure with the increment of the inter-slit distance (D) of nanograting from 800 to 1100 nm [45]. Copyright 2013, Springer Nature.

structures, and thereby, the moving distance of hot electrons toward metal–semiconductor interfaces might be reduced. Figure 7I reveals the measured spectral photoresponsivity of the active optical antenna-based device with gold nanograting structures. The maximum photoresponsivity of the device with gold nanograting structures is up to approximately 600 nA mW^{-1} at zero bias voltage in the IR regime, which is approximately 10 times higher than the previous report. Furthermore, the responsivity peak can be tuned readily by adjusting the feature size of gold nanograting structures on the active optical antenna-based devices [Figure 7I]. Accordingly, Sobhani et al. have experimentally demonstrated that the increment of absorption of plasmonic nanostructures close to metal–semiconductor junctions can essentially decrease the moving distance of hot electrons toward Schottky barrier to improve the photoresponse of the active optical antenna-based devices.

Active optical antenna-based devices featuring distinct plasmonic nanostructures, including nanorods [41], nanowires [42], and nanogratings [45], have been discussed intensively so far. Typically, these plasmonic nanostructures have the feature dimensions in the range from several tens to hundreds of nanometres. Thus, they are fabricated by FIB or EBL in general. Furthermore, these plasmonic nanostructures generally feature the properties of localized surface plasmon resonances. However, the nature of LSPR and the properties of nanograting structure indicate that the active optical antenna based on these plasmonic nanostructures might intrinsically response to only certain polarizations of light and feature narrow-band photoresponses [45]. Therefore, many critical challenges remain to develop an active optical antenna-based device that can not only possess high photoresponsivity and detectivity over a broadband wavelength regime below the band edge of semiconductor materials but also perform identical photoresponse toward randomly polarized light.

In order to overcome these challenges, Lin et al. proposed and experimentally demonstrated the concept of integrating deep trench/thin metal (DTTM) antenna into Si-based devices to achieve high-photoresponsivity and polarization-insensitive photodetection at telecommunication wavelengths [44]. Figure 8A presents the schematic illustrations of the DTTM antenna on the Si substrates. The DTTM antenna-based device is composed of a single layer of gold film with a thickness of 30 nm on a three-dimensional (3D) trench-like-structured Si substrate. In this design, the DTTM antenna could provide a large area of metal–semiconductor junctions (Figure 8B) to improve the propagation paths of generated hot electrons. Furthermore, the DTTM antenna structure provides high-intensity electric fields around the structure and performs a good absorption capability over

the broad bandwidth (Figure 8C). The peak absorption of the DTTM antenna is as high as approximately 88% in the IR regime, which is several times to one order of magnitude higher than those of previously reported plasmonic nanostructures. In addition, as displayed in Figure 8D, the DTTM antenna could well confine the incident IR light in the trench-like structures at both polarization states (*x*- and *y*-polarizations). Therefore, the DTTM antenna presents a polarization-insensitive absorption capability in the IR regime. Based on these attractive properties of DTTM antenna, they enable high photoresponsivity devices over a broad bandwidth at zero bias voltage. As displayed in Figure 8E, the photoresponsivities of DTTM antenna-based devices are two orders of magnitude higher than those of the active optical antenna-based devices featuring nanorods. Furthermore, the DTTM antenna-based devices present an excellent detection linearity even under illumination with low-intensity light at a wavelength of 1550 nm. Accordingly, combining the functions of the enhancement of absorption of plasmonic nanostructures and increment of the area of metal–semiconductor junctions together has been experimentally demonstrated, which can significantly improve the photoresponses of active optical antenna-based device. This strategy can not only dramatically increase the total number of plasmon-induced hot electrons in the structured metal layer but also efficiently transport the generated hot electrons into the conduction band of semiconductor materials.

To further improve the photoresponsivities of active optical antenna-based devices, Lin et al. proposed a concept of using an embedded trench-like (ETL) antenna-based device for photodetection in the IR regime [43]. As displayed in Figure 9A, the components of the ETL antenna-based device are similar to that of DTTM-based device. The main difference between these two active optical antenna-based devices is the operation methodology. For active optical antenna-based devices, the incident light would generally propagate through the plasmonic nanostructures to the semiconductor materials (Figure 9B). In contrast, for ETL antenna-based device, the incident light, which has the photon energy lower than the bandgap of semiconductor materials, could directly transmit through the semiconductor materials, and then interact with the plasmonic nanostructures (Figure 9A). Therefore, most of the incident light would be absorbed by the structured metal layer close to metal–semiconductor interfaces (Figure 9C). In other words, the plasmon-induced hot electrons would be generated very close to metal–semiconductor interfaces in this operation methodology. Accordingly, the moving distance of hot electrons could be effectively reduced to essentially decrease their collision probabilities in the metal layer. In general, Si features high indices of approximately 3.48 in the

Figure 8: (A) Schematic representation and (B) top-view and cross-section SEM images of the active optical antenna-based device featuring DTTM antenna. (C) Simulated absorbance spectra of different plasmonic nanostructures, including DTTM antenna, nanorods, dot arrays, and hole arrays. (D) The electric field distributions of the light at the wavelengths of 1420 and 1550 nm propagating through the DTTM antenna structure on a Si substrate. (E) Measured spectral responsivities of the DTTM antenna-based devices featuring different dimensions of hole and period and those of the active optical antenna-based devices featuring different lengths of nanorods [44]. Copyright 2014, Springer Nature.

IR regime. When light with wavelengths from 1250 to 1650 nm (in air) transmits into Si, the effective wavelengths of light would be significantly shortened to be around 360 to 475 nm (in Si). Compared with DTTM antenna-based devices, light in Si would be well confined within the ETL antenna-based devices and then be gradually absorbed by the structured metal layer. Therefore, the ETL antenna performs a better absorption capability (>80%) than the DTTM antenna over a broad wavelength regime (Figure 9D). Accordingly, the photoresponsivities of ETL based devices

are 2–5 times higher than those of DTTM based devices as displayed in Figure 9E. In addition, the ETL based devices perform omnidirectional photodetection capability at telecommunication wavelengths. As displayed in Figure 9F, the measured photoresponses of ETL based devices at the wavelengths of 1310–1550 nm and various incident angle of light are varied within 10%. An active optical antenna-based device for high-photoresponse, omnidirectional, and polarization-insensitive photodetection well below the band edge of semiconductor materials has been successfully demonstrated.

In addition to structured active antenna-based devices, Wang et al. recently proposed and experimentally demonstrated a concept of using planar hot-electron device, which consists of metal and dielectric thin film layers, to achieve wavelength selective photodetection at NIR regime via Tamm plasmon [39]. Figure 10A and B displays the schematic representation and SEM image of the planar Tamm plasmonic (TP) hot-electron device. The TP structure comprises of an Au/Ti-ZnO-ITO structure and a modified Ge/SiO₂ distributed Bragg reflector. The incident light can be highly confined at the Au layer and close to the Ti-ZnO interface to enhance the absorption of Au film at the wavelength of the

TP resonance (Figure 10C). Therefore, the TP structure exhibits a sharp and narrow absorption peak (absorption ~70%) at the TP resonance wavelength (Figure 10D). The TP plasmon-induced hot electrons feature enough energy to across the barrier height of Au/Ti-ZnO (Figure 10E), and thus, contribute to photocurrent. Figure 10F displays the spectral photoresponse of the planar TP hot-electron device. The device can detect the electromagnetic energy well below the band edge of ZnO with a peak responsivity of 8.26 nA mW⁻¹ at the wavelength of 1581 nm. This new concept of planar hot-electron device provides a lithography-free strategy to achieve wavelength selective photodetection via

Figure 9: Schematic illustrations of the optoelectronic behaviors of (A) ETL antenna-based device and (B) most of active optical antenna-based devices under IR illumination. (C) Absorption map of the ETL antenna-based device at a wavelength of 1310 nm. (D) Simulated absorbance spectra and (E) measured spectral photoresponsivity of the ETL antenna-based and DTTM antenna-based devices. (F) Measured photocurrents of ETL antenna-based device at different angles of incidence and wavelengths of 1310 (black line) and 1550 nm (red line) [43]. Copyright 2019, American Chemical Society.

Tamm plasmon [39, 119–121] and have a great potential for use in many applications of telecommunications.

In summary, active optical antenna-based devices, which featuring plasmonic nanostructures, such as nanorod, nanowire, nanograting, micropillar, metamaterial, disordered nanocomposite, random gold nanoparticles and trench-like antenna, on semiconductor materials, and planar TP hot-electron device have been demonstrated for photodetection well below the band edge of semiconductor materials. Table 1 compares the structure types, used materials, and photoresponsivity of the previously reported active antenna-based photodetectors and planar TP hot-electron devices operating at telecommunication wavelengths. The responsivities of these hot electron-based devices are in the range of 8 and 5854 nA mW⁻¹ and 1.5 and 1400 nA mW⁻¹ at zero bias voltage and the wavelengths of 1310–1550 nm, respectively.

Many factors, including the absorption of plasmonic nanostructures and the contact area between structured

metal layer and semiconductor materials, might significantly influence the performances of the active optical antenna-based devices. In addition, the active optical antenna-based devices featuring polarization-insensitive and omnidirectional photodetection capability also have been experimentally demonstrated. Nevertheless, the photoresponsivities of the previously reported devices are still much lower than those of Ge- and III–V semiconductor materials-based devices in the IR regime. Furthermore, the noble metals, e.g., Au, are not compatible with the CMOS manufacturing processed in general. Therefore, the challenges remain in the development of active optical antenna-based devices featuring high photoresponsivities in the IR regime through the mature CMOS technology. The CMOS-compatible materials and novel 2D materials (e. g., graphene) [125–127], which have been demonstrated featuring fast plasmon-induced hot electron transfer capability [127], should be taken into considerations for the design of active optical antenna-based devices.

Figure 10: (A) Schematic representation and (B) SEM image of the planar TP hot-electron device. (C) Absorption map of the planar TP device at the wavelength of 1600 nm. (D) Simulated reflection and absorption spectra of the planar TP device. (E) Energy band diagram of the TP hot-electron device. (F) Spectral photoresponse of the planar TP hot-electron device [39]. Copyright 2019, The Royal Society of Chemistry.

Table 1: Properties (structure types, used materials, and photoresponsivity) of recently reported active antenna hot electron-based devices.

Active antenna-based device			Photoresponsivity (at zero bias voltage)	
Structure type	Material	Ref.	$\lambda = 1310 \text{ nm}$ (nA mW^{-1})	$\lambda = 1550 \text{ nm}$ (nA mW^{-1})
Nanorod	Au/Si	[41]	ca. 8	ca. 1.5
Nanograting	Au/Si	[42]	ca. 580	ca. 75
Metamaterial perfect absorber	Au/Si	[37]	ca. 2800	
Chiral metamaterial	Ag/Si	[36]	ca. 2100	
Disordered nanocomposite	Au/Si	[122]	5100	1400
Random gold nanoparticles absorber	Au/Si	[123]	ca.1500	ca. 140
Planar Tamm plasmonic structures	Au/Ti/ZnO	[39]		ca. 3
Deep trench/ thin metal (DTM) structure	Au/Si	[44]	2688	167
Embedded trench-like (ETL) structure	Au/Si	[43]	5854	693
Micropyramid	Au/Si	[124]	ca. 1800	ca. 200

4 Strategy III: Thermoplasmonic effects of plasmonic nanostructures

Thermoplasmonics is based on the utilization of electromagnetic waves absorbed by the plasmonic nanostructures through plasmon resonances to modulate the temperature of plasmonic nanostructures [46–48, 51]. The thermoplasmonic effects have been widely used in many applications, such as seawater desalination, solar energy harvesting [52–55, 67, 101, 128], photodetection [68], and photothermal therapeutics [58–64]. In general, the plasmonic nanostructures are contacted with a medium (e. g., water and photovoltaic devices) to conduct the photogenerated heat for subsequent applications, for example, heating the medium or converting the photothermal energy into other forms of energy (e. g., electricity). Liu et al. have demonstrated that the self-assembled Au NPs film on paper substrate can be used in seawater desalination system for large-scale water evaporation under the illumination of sunlight [125].

Figure 11A displays the schematic representation of the structure of the air laid-paper-based AuNPs (PGF). The plasmonic AuNPs film converts the incident solar energy into thermal energy as a solar energy trapping layer and generates hot zone at the air-water interfaces. The underlying paper substrate provides a good mechanical stability and low thermal conductivity as a support for the plasmonic AuNPs film [Figure 11B]. The low thermal conductivity of paper can prevent the photogenerated heat directly transfer from AuNPs film to bulk water as a thermal insulator. Furthermore, the large amounts of micro-pore structures within the air laid-paper substrate can rapidly transport water to the hot zone by capillary. Therefore, the photogenerated heat can be effectively used in the hot zone for water evaporation. Figure 11C displays the measured

absorption spectra of PGF. Most of solar light in visible regime can be absorbed (>80%) by PGF. Such high absorption enables PGF to effectively harvest solar energy for the conversion of thermal energy. Figure 11D displays the surface temperature distributions of PGF before and after the illumination of sunlight. After illumination at a power density of 4.5 kW m^{-2} for 15 min, the surface temperature of PGF increased from room temperature (27°C) to 80°C (Figure 11D). The high surface temperature of PGF is attributed to the localized plasmonic heating induced by the plasmonic nanostructures and the thermal insulation by the air laid-paper. Accordingly, the evaporation efficiency of PGF is as high as 77.8% under solar illumination [Figure 11E].

To further improve the solar evaporation efficiencies of plasmonic nanostructures, Zhou et al. proposed a concept of using 3D self-assembled aluminum NPs [66] for plasmon-enhanced solar water evaporation (Figure 12A). As displayed in Figure 12B, this plasmonic nanostructure is composed of Al NPs with random sized and structured anodic aluminium oxide (AAO) membrane, which named Al NP/AAM structure. The nanoporous AAO membrane provides an impedance match for efficient reflection reduction and coupling to the optical modes. Furthermore, Al NPs with random sizes and distributions located at the sidewalls of AAO membrane enable a high density of hybridized LSPR to absorb light over a broad wavelength regime. Therefore, this plasmonic nanostructure performs an average absorbance of >96% from visible to NIR regimes (Figure 12C). Furthermore, the photogenerated heat on the surface of Al NP/AAM structure can be efficiently transfer to the water for steam generation since the photogenerated heat just need to heat up a small amount of water inside the nanoporous membrane. Accordingly, the solar steam efficiency of the Al NP/AAM structure is as high as approximately 90% under solar illumination with the concentration factor of 6 (Figure 12D). In addition, the

Figure 11: (A) Schematic representation of the airlaid-paper-based AuNPs (PGF). (B) The low- and high-magnification SEM images of PGF. (C) Measured absorption spectra of PGF and free-standing Au NPs film. (D) The surface temperature distributions of PGF before and after the illumination of sunlight at the power density of 4.5 kW m^{-2} . The thermal images were recorded by IR camera. (E) The time-dependent maximum, minimum, and average weight changes using PGF under the illumination of sunlight [125]. Copyright 2015 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

quality of the evaporated water, which collected from solar vapor evaporation, is very good. As displayed in Figure 12E, the salinity levels, which defined by World Health Organization and the US Environmental Protection Agency standards, of the evaporated water are several orders of magnitude lower than those of seawater before the solar desalination process. Furthermore, the concentrations of ions (e. g., Na^+ , K^+ , Mg^{2+} , Ca^{2+} , and B^{3+}) in the seawater could be reduced significantly after solar desalination process (Figure 12F). Due to the scalable fabrication process and low cost for the metallic NPs-stacked structures, this plasmonic nanostructures could be a portable solution for solar desalination without carbon footprint [65, 66].

In addition, the integration of plasmonic nanostructures with heat-sensitive devices can indirectly convert electromagnetic radiation into electricity through thermoplasmonic effects [56, 67]. For the operation methodology of this type of devices, the incident light would firstly be converted into thermal energy through the plasmonic nanostructures and then indirectly converted into electrical signals using a heat-sensitive device. Compared with traditional semiconductor-based optoelectronic devices [86, 96, 129, 130], the major advantage of these devices is that the electrical signals are derived from the photogenerated thermal energy, allowing for the conversions of certain or broadband electromagnetic energies. Therefore, the plasmonic nanostructures featuring

tailorable absorption properties across the entire electromagnetic spectrum have a great potential for use in thermoplasmonic-based devices for many applications (e. g., energy harvesting and photodetection). Kosuga et al. have demonstrated that Au nanoparticle-fixed beads (Au NP-FB) exhibit a superior photothermal performance and this plasmonic nanostructure can further be integrated with a thermoelectric device for solar thermoelectric energy conversion [56]. Figure 13A and B displays the schematic representation and SEM images of the plasmonic solar thermoelectric device, respectively. They coated the Au NP-FB film on the top surface of n-type and p-type thermoelectric devices. As displayed in Figure 13A, the Au NP-FB film is hot side of the plasmonic solar thermoelectric device that would first convert the incident solar energy into thermal energy. Then the photogenerated heat further converts into electricity by the underlying thermoelectric materials (cold side). Figure 13C displays the extinction spectra of the Au NP-FB film. Such wide extinction spectra enable the Au NP-FB film to effectively convert solar energy to thermal energy. Thus, the Au NP-FB film exhibits a superior photothermal performance. As displayed in Figure 13D, the temperature of Au NP-FB film can be increased to 68.4°C after 100 s under artificial sunlight irradiation, resulting in the difference in temperature of 43.4°C . Therefore, the thermoelectric devices based on plasmonic Au NP-FB film generate electrical signals in the form of

Figure 12: (A) Schematic representation and (B) top-view and cross-section SEM images of the Al NP/AAM plasmonic nanostructures. (C) Simulated and experimental absorption spectra of the Al NP/AAM plasmonic nanostructures. (D) The evaporation performance of an Al NP/AAM structure under different solar concentrations. (E, F) The measured (E) salinities (the weight percentage of Na^+) of the four seawater samples and (F) concentrations of four ions in the seawater before and after desalination. The dashed coloured lines refer to the World Health Organization and the US Environmental Protection Agency standards for the drinkable water [66]. Copyright 2016, Springer Nature.

voltage when there are different temperatures on each side under illumination of sunlight [Figure 13E].

Although the plasmonic nanostructures featuring LSPR properties perform superior photothermal characteristics, the thermal resistance at the interface between materials might result in heat loss during the process of conduction. On the other hand, the photogenerated heat in plasmonic nanostructures cannot be completely transferred to the contacted heat-sensitive devices. Therefore, the challenge remains to develop a plasmonic-based device that can directly convert the photogenerated heat to electrical signals through the plasmonic nanostructures. Lin et al. proposed a concept of using a single layer trench-

like metal film for color image sensing [68]. As displayed in Figure 14A, the structured metal layer can efficiently absorb light to immediately generate heat through SPR and cavity effects, and then conduct the photogenerated heat through the continuous metallic structures at the resonant wavelengths. In contrast, the trench-like metal film reflects most of incident light at non-resonant wavelengths. Only small amount of thermal energy will be generated at the non-resonant wavelengths. Therefore, the trench-like plasmonic nanostructures perform not only an excellent color selective absorption capability (Figure 14B) but also good photothermal conversion abilities at the resonant wavelengths (Figure 14C). The photogenerated heat in the

plasmonic nanostructures would subsequently lead to the change of resistance of structured metal layer (Figure 14D). In other words, the trench-like plasmonic nanostructures can directly convert the photon energy to electric signals through thermoplasmonic effects. Also, the trench-like nanostructures have been experimentally demonstrated featuring photoresponses toward particular color (Figure 14E) due to their color selective absorption characterizations. Therefore, a single-layer trench-like structured metal film provides such attractive filter-free and junctionless properties, suggesting it has a great potential for use in the development of devices possessing photoresponses towards any designed wavelengths.

As discussed above, the developed plasmonic nanostructures generally feature efficient and broadband absorbance, and good photothermal performance suggesting they are promising for many applications in electromagnetic energy harvesting fields such as solar desalination, solar

thermal energy conversion, and solar thermophotovoltaics (STPV). Among these energy harvesting fields, STPV has been extensively investigated recently due to the theoretical analysis predicting its efficiencies can reach up to 85%. However, the working temperatures of STPV systems require at least 800 °C and normally in the range from 900 to 1300 °C. This high temperature range presents a significant challenge for plasmonic absorbers based on noble metals, which generally suffer from the problem of low melting points, especially in the nanoscale where the melting point would be greatly decreased. For example, the melting points of Au, Ag, and Al are 1046, 961, and 660 °C, respectively. Therefore, metals featuring high melting point, such as W, which possesses a melting point as high as 3400 °C, would be a good candidate as refractory materials for optical absorbers [131–133]. Han et al. demonstrated a tungsten-based solar selective absorber for broadband and polarization-insensitive solar energy harvesting [132]. Figure 15A and B displays

Figure 13: (A) Schematic representation of the solar thermoelectric device based on plasmonic Au nanoparticle-fixed beads (Au NP-FB). (B) SEM images of Au NP-FB film. (C) Measured extinction spectra of Au NP-FB film, Ag NP-FB film, single Au NP, and single Ag NP. (D) Correlation between temperature and time of the Au NP-FB, Ag NP-FB film, and single Au NP under illumination of sunlight and after turning the light off. (E) Power generation properties of the solar thermoelectric device based on plasmonic nanostructures after 5 min under artificial sunlight irradiance [56]. Copyright 2015, Royal Society of Chemistry.

the schematic representation and SEM image of the tungsten-based absorber, which comprises periodic tungsten nanodisk array on a SiO_2 layer/tungsten film stack. This tungsten-based absorber presents excellent solar selection absorption capability. As displayed in Figure 15C, the absorption of absorber is more than 90% in the wavelength regime from 500 to 1750 nm and drops to less than 12.6% beyond the wavelength of 2500 nm. Furthermore, this tungsten-based absorber can maintain the solar selective absorption even when the incident angle is up to 40°

(Figure 15D). Therefore, the tungsten-based solar selective absorber has a great potential for use in the practical high-temperature solar thermal energy harvesting. In addition to tungsten, titanium nitride (TiN) featuring a melting point of 2930°C , great thermal stability, and CMOS compatibility is a candidate for high-temperature energy harvesting [134, 135]. Chirumamilla et al. demonstrated a large area ultra-broadband 3D TiN nanopillars absorber for solar thermophotovoltaics [134]. Figure 15E and F displays the schematic representation and SEM image of the TiN nanopillars

Figure 14: (A) Schematic representation of the photothermal behaviors of trench-like structured metal film at resonant and non-resonant wavelengths. (B) Measured absorption spectra of trench-like structured metal film having different structural parameters. (C) Correlation between temperature and time for the trench-like structured metal film having hole of 270 nm and period of 600 nm in the dark and under illumination of light with power density of $1.1\ \text{W cm}^{-2}$. (D) Resistance of trench-like structured metal film at different temperatures. (E) Spectral photoresponsivity of the trench-like structured metal film having different structural parameters measured at a bias voltage of 0.1 V [68]. Copyright 2016, Royal Society of Chemistry.

absorber. The TiN-based absorber comprises single layer TiN film with a thickness of 90 nm on structured Si nanopillars. TiN nanopillars absorber exhibits not only ultrabroadband absorption (300–2300 nm) but also excellent thermal stability. As displayed in Figure 15G, the absorptions of the TiN nanopillars with and without high-temperature thermal treatments at 1473 K retain almost the same. Therefore, these refractory absorbers have a great potential for use in high-temperature energy conversion applications, such as STPV, waste heat harvesting, and highly concentrated solar thermal power plants.

In addition, carbon-based materials (e. g., graphene metamaterials) with low-cost and scalability, have been extensively investigated with plasmonic nanostructures and demonstrated impressive broadband dispersionless nature, tunable bandgap, and excellent thermal conductivity [101, 102, 128, 136, 137]. In 2019, Lin et al. proposed a 90-nm-thick graphene grating metamaterial for strong and ultrabroadband absorption

of unpolarized light [101]. Figure 16A and B displays the schematic representation and top-view SEM images of the graphene grating metamaterial absorber. They used laser writing method to directly fabricate the designed grating structure, which featuring period of 980 nm and width of 500 nm, on the graphene metamaterial. This graphene grating metamaterial presents high absorptions (>80%) in the broad wavelength range from 300 to 2500 nm (Figure 16C) even when the thickness of the graphene metamaterial is only 90 nm. Therefore, the graphene grating metamaterial absorber performs extraordinary photothermal performance under the illumination of natural sunlight as displayed in Figure 16D and E. The temperature of graphene grating metamaterial absorber can increase significantly to approximately 160 °C within 1 min under sunlight (Figure 16E). Therefore, this concept opens new avenues for applying 2D materials to enable novel and functional optoelectronic devices for energy harvesting.

Figure 15: (A) Schematic representation and (B) top-view SEM image of tungsten-based absorber. (C) Simulated and measured absorption spectra of tungsten-based absorber. (D) Measured spectral absorption of tungsten-based absorber under different angles of incidence of 8, 20, 40, and 60° [132]. Copyright 2017, Optical Society of America. (E) Schematic and (F) SEM image at 54° tilted view of 3D TiN nanopillars absorber. (G) Measured absorption spectra of TiN nanopillars absorber before and after annealing at 1473 K [134]. Copyright 2017, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Figure 16: (A) Schematic representation, (B) top-view SEM images, and (C) measured absorption spectra of the graphene grating metamaterial absorber. (D) Thermal image of the graphene grating metamaterial absorber under illumination of natural sunlight. (E) Temperatures of the graphene grating metamaterial absorber after 130 s of sunlight illumination [101]. Copyright 2019, Springer Nature. (F) Schematic representation and (G) top-view SEM images of the SGM absorber. (H) Simulated and measured absorption spectra of the SGM absorber with different structural parameters. (I) Thermal image of the SGM absorber under illumination of artificial sunlight in an open environment. (J) Temperatures of the SGM absorber after 5 min of illumination. (K) Measured absorption spectra of the SGM absorber before and after annealing at 100 °C in air [136]. Copyright 2020, Springer Nature.

Carbon-based materials generally possess high absorption over broad wavelength regime, which means they do not have spectral selective mechanism and face the high thermal emission loss. Recently, Lin et al. proposed and experimentally demonstrated that the graphene-based metamaterials could be conformally coated on the plasmonic nanostructures by a solution-phase film deposition technique [136]. The proposed structured graphene metamaterial (SGM) absorber can sufficiently improve the solar energy collection efficiency and reduce the thermal radiation loss to achieve high-efficiency solar thermal energy harvesting. Figure 16F and G displays the schematic representation and top-view SEM image of the SGM solar selective absorber. The SGM absorber presents superior solar selective absorption and flexible tunability of wavelength selective absorption as displayed in Figure 16H. Furthermore, the SGM absorber performs excellent photothermal performance and high thermal stability. As displayed in Figure 16I and J, the temperature of SGM absorber can increase significantly to approximately 83 °C under artificial sunlight with power density of 100 mW cm⁻². In addition, the absorptions of the SGM absorber with and without thermal treatments at 100 °C retain almost the same over broad bandwidth (Figure 16K). Therefore, the integration of graphene-based materials with plasmonic nanostructures would be

a new research perspective for the development of high-efficiency thermo-plasmonic devices.

In summary, many different plasmonic nanostructures have been widely used in the fields of solar energy harvesting, solar desalination, solar thermal energy conversion, STPV, and photodetection, through their photothermal features. Table 2 compares the structure types, used materials, absorbance, and temperatures under illumination of previously reported electromagnetic absorbers operating in the UV, visible and NIR regimes. This strategy allows tailorable photon energy collection across the full electromagnetic spectrum of the sun. In general, the absorptions of the absorber are higher than 90% at the designed wavelengths. Furthermore, the temperatures of these absorbers are in the range of 68.4 and 210 °C, which are mainly depending on the absorption and thermal conductivity of the absorber, thermal property of the substrate and power density of illumination. Efficient and tunable absorbance across the electromagnetic spectrum, the reduction of thermal resistance between materials and thermal radiation loss, and the improvement of effective uses of photogenerated thermal energy through the materials with high thermal conductivity and stability (e. g., graphene metamaterials [136]), are the main aspects for the development of high-efficiency energy conversion plasmonic-based devices.

Table 2: Properties (structure types, used materials, absorbance, and temperature) of recently reported electromagnetic absorbers.

Structure type	Material	Absorbance (@Wave-length)	Temperature (@ power density of illumination)	Ref.
Nanoantenna metamaterial	Ag/SiO ₂ /Au	ca. 1 (@ 730 nm)		[138]
Crossed gratings metamaterial	Ag/SiO ₂ /Ag	ca. 0.8 (@477 nm)		[18]
Nanoparticles metamaterial	Au/SiO ₂ /Au	ca. 0.89 (@400-700 nm)		[139]
Nanocomposite	Au/silk	> 0.95 (@350-750 nm)	ca. 100 °C (@200 mW cm ⁻² of LED lamp)	[67]
Gold NP-FB	Au		68.4 °C (@100 mW cm ⁻² of artificial sunlight)	[56]
Airlaid-paper-based AuNPs (PGF)	Au	> 0.8 (@400-800 nm)	80 °C (@450 mW cm ⁻² of artificial sunlight)	[125]
Al NP/AAM plasmonic nanostructures	Al/AAM	> 0.8 (@400-1900 nm)		[66]
Au NP/nanoporous templates (NPTs) plasmonic absorber	Au/NPTs	> 0.9 (@200-2500 nm)		[65]
Nanopyramid solar absorber	Ni	> 0.8 (@300-1800 nm)		[53]
Nanodisk metamaterial	W/SiO ₂ /W	> 0.9 (@500-1750 nm)		[132]
Nanopillars	TiN	> 0.8 (@300-2300 nm)		[134]
Nanocone metamaterial	TiN/Al ₂ O ₃ /TiN	> 0.95 (@400-1500 nm)		[135]
Loading effect-induced broadband absorber	Al	> 0.8 (@ca.510-820 nm)	210 °C (@3 W cm ⁻² of Xe lamp)	[54]
Graphene grating metamaterial	Graphene/ SiO ₂ /Ag	> 0.8 (@300-2500 nm)	160 °C (@ natural sunlight)	[101]
Structured graphene metamaterial (SGM) selective absorber	GM/Cu	> 0.85 (@280-1550 nm)	83 °C (@100 mW cm ⁻² of artificial sunlight)	[136]

5 Conclusions

Overall, the fundamental mechanism and characteristics of plasmonic nanostructures, such as the enhancement of electric fields, the generation of hot electrons, and thermoplasmonic effects, have been intensively investigated and applied into many areas in sensing, energy harvesting and photodetection. Recently, these plasmonic nanostructures have been successfully integrated with diverse devices for use in many practical applications, such as SERS sensors, solar photovoltaic and solar thermal cells, IR photodetectors, solar desalination, and color image sensors, for the improvement of efficiencies and sensitivity of the devices, and the extension of detection bandwidth well below the band edge of semiconductor materials. Therefore, this technology has a great contribution to both fundamental science and practical applications in the real life.

This review summarizes the fundamental mechanism of plasmonic nanostructure devices, highlighting the state-of-the-art development and several major challenges that need to be further addressed despite the current exciting achievements and the enormous potential. For the perspectives on photodetection and energy conversion, photothermal effect of plasmonic nanostructures feature to be a promising solution for the conversion of electromagnetic radiation with high efficiency due to the fact it can utilise the electromagnetic energy over the entire solar spectrum. By using photothermal effect, incident light could be first converted into thermal energy, and then converted indirectly into electric energy using a thermoelectric device. The major advantage of this approach is that the electrical signals are derived from the photogenerated heat, allowing broadband photon-energy conversion. However, most of the plasmonic nanostructures composed of noble metals would not be suitable to work under high temperatures because the melting points of the noble metals are generally low, in particular at the nanoscale dimensions where the melting point of noble metals would be greatly decreased. Although several refractory absorbers, such as tungsten- and TiN-based absorbers, featuring broadband absorption have been proposed and demonstrated, their photothermal characteristics have been rarely explored and remained unclear. Therefore, developing new types of materials, construction of novel nanostructures, and investigations on their photothermal properties would be essential topics in the development of refractory absorbers. Furthermore, how to develop a refractory plasmonic nanostructure featuring efficient and broadband absorption, tailorable photothermal behaviors, and wide

operating temperature ranges would also be a worthwhile topic to explore. In addition, in recent years, many novel nanomaterials (e. g., graphene, MoS₂, and perovskite) have been proposed and experimentally demonstrated. The plasmonic properties of these new nanomaterials have largely remained elusive and would be another interesting direction in the study of plasmonics and nanophotonics.

On the other hand, integrating the structured nanomaterials with tailored plasmonic properties into devices while exploiting their original functionalities (e. g., high thermal conductivity of graphene) remains challenging but crucial for device performance. Several challenges will be faced during the integration processes, including how to conformally coat the nanomaterials on plasmonic nanostructures, pattern the nanomaterials on substrates with minimum damage, and retain the stability of nanomaterials during the fabrication and integration processes. In addition, the feature sizes of plasmonic nanostructures are generally in the range from several tens of to hundreds of nanometers. Therefore, plasmonic nanostructures are typically fabricated using complicated and expensive manufacturing processes, such as FIB and EBL. The development of low-cost, high-throughput, and scalable manufacturing methods to produce plasmonic nanostructures and integrate them into the devices would be vital for promoting plasmonics as viable sensing, photodetection and energy conversion technology. We hope this review, along with the outstanding literatures in the field of plasmonics, will promote the research in this area and facilitate the realization of plasmonic nanostructures and devices in the real life.

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