Review

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Active plasmonic nanoantenna: an emerging toolbox from photonics to neuroscience

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Abstract: Concepts adapted from radio frequency devices have brought forth subwavelength scale optical nanoantenna, enabling light localization below the diffraction limit. Beyond enhanced light–matter interactions, plasmonic nanostructures conjugated with active materials offer strong and tunable coupling between localized electric/electrochemical/mechanical phenomena and far-field radiation. During the last two decades, great strides have been made in development of active plasmonic nanoantenna (PNA) systems with unconventional and versatile optical functionalities that can be engineered with remarkable flexibility. In this review, we discuss fundamental characteristics of active PNAs and summarize recent progress in this burgeoning and challenging subfield of nano-optics. We introduce the underlying physical mechanisms underpinning dynamic reconfigurability and outline several promising approaches in realization of active PNAs with novel characteristics. We envision that this review will provide unambiguous insights and guidelines in building high-performance active PNAs for a plethora of emerging applications, including ultra-broadband sensors and detectors, dynamic switches, and

large-scale electrophysiological recordings for neuroscience applications.

Keywords: active plasmonics; functional plasmonics; nanoantenna; nanocircuit; neurophotonics; plasmonics.

1 Introduction

Plasmonics is a rapidly growing field at the nexus of photonics, electronics, and nanotechnology [1]. Plasmonic nanostructures have opened up extraordinary ways to guide and localize electromagnetic fields at physical dimensions smaller than the wavelength of light [2, 3]. By exploiting coherent excitations of conduction electrons at metallic surfaces, they bridge the gap between the diffraction limited optics and nanoscale phenomena [2–8]. By creating local hotspots of the electric field at the nanometer scale, plasmonic nanostructures enhance light–matter interactions by several orders of magnitude [9], paving the way to reinvention of the most known optical phenomena with previously unthinkable ways [10]. During the last couple of decades, we have witnessed transformative breakthroughs in a myriad of different research areas ranging from next-generation photovoltaic devices [11–15] and subdiffraction-limited imaging [13, 16–18] to ultrasensitive biosensing [13, 16, 19–24] and photodynamic cancer therapy [13, 16]. Over the years, an enormous amount of effort has been devoted to the development of large-scale and low-cost nanofabrication techniques [21, 25, 26] with the goal of transitioning plasmonic technologies from research laboratories to the industry [27–29].

Plasmonic modes of metallic nanostructures can be classified into two distinct types: surface plasmon polaritons (SPPs) and localized surface plasmon polaritons (LSPs) [30]. SPPs are propagating bound oscillations of electrons and electromagnetic waves at a metal–dielectric interface. In contrast, LSPs are standing wave surface plasmons that are tightly confined on subwavelength nanoparticle surfaces [30]. Incident light in resonance with coherent electron oscillations leads to localized surface plasmon resonance (LSPR) [30]. Utilizing surface-confined

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plasmonic excitations, optically resonant nanoparticles can funnel electromagnetic energy from continuum to local nanometer volumes and subsequently radiate it back to the continuum with high efficiencies [31]. Electromagnetic coupling between the localized excitations and free-space radiation enabled by the plasmonic nanoparticles is analogous to that of conventional radio frequency (RF) antennas. Hence, plasmonic nanostructures are frequently referred to as plasmonic nanoantennas (PNAs) [31–36]. Thanks to their unparalleled ability to control light–matter interactions at deep subwavelength scale, PNAs have emerged as an effective tool for a multitude of emerging technological applications, including solar energy harvesting [37, 38], sensing [39–41], nanomedicine [42], imaging [43], communication [44, 45], spectroscopy [26, 46–49], single-molecule analysis [50, 51], optical trapping [52], light emission [53–57], photocatalysis [58–60].

Despite recent advances, PNAs are conventionally devised for single-purpose use, meaning that their optical properties are predetermined through the design and manufacturing process. This presents a major hurdle for many practical applications that require a dynamic optical response. Active control over individual nanoantenna characteristics is inevitably needed for the advancement of future plasmonic technologies such as optical modulators [61–64], switches [65–68], and field-effect neuromorphic devices [10, 69]. Dynamically reconfigurable plasmonics, commonly referred to as “active plasmonics” [70, 71], has attracted remarkable interest since the term coined in 2004 [72]. As evident by the rapidly increasing number of annual citations to active plasmonics–related scientific articles (Figure 1), this new research field continues to grow at an outstanding pace. Progress in this field has already facilitated development of novel active plasmonic devices with

unprecedented photon management capabilities, leading to new physical phenomena and a broad range of new exciting practical applications [10, 73, 74]. Beyond their passive counterparts, active PNA technologies have shown remarkable characteristics, enabling researchers to achieve new device functionalities, including ultraprecise gas sensing [73] and wireless electrophysiological recordings at the diffraction limit of light [10].

Here, we discuss the latest and most critical findings in active plasmonics and provide an overview of active PNA devices. This review is organized as follows: we first summarize the basic principles underlying PNAs and their general properties. Subsequently, we discuss a powerful and universal inverse design approach for rapid and efficient engineering of PNAs with high quality factor and narrow linewidth resonance characteristics. We then highlight two advanced nanofabrication techniques enabling high-throughput, large-scale manufacturing of PNAs with remarkably high structural uniformity at wafer scale. Later, we describe an elegant optical nanocircuit framework enabling parametrization of sophisticated optical characteristics of active PNAs. In the following section, we use optical nanocircuit theory to group active plasmonic approaches into three fundamentally different categories, providing general guidelines for rational device design. Finally, we introduce ultrasensitive electro-active PNAs for electrophysiological applications and discuss the emerging field of plasmonic neuromorphic devices with potential future directions.

2 Metallic plasmonic nanoantennas

Metallic PNAs are one of the most commonly used structures in the nanophotonic toolbox due to the ease of their engineering [35, 75, 76]. PNAs allow light manipulation at subwavelength scales and enable enhanced electron–photon coupling [30]. Inspiration for these optical antennas can be traced back to their radiowave and microwave counterparts (Figure 2A). Electrical antennas driven by high-frequency voltage sources induce oscillations of currents (oscillating polarization), leading to radiowave and microwave radiation. Analogously, when driven by high-frequency “optical sources”, oscillations of “optical current” can be induced in PNAs, yielding plasmonic oscillation in the spectral range spanning from ultraviolet (UV) to visible and near-infrared frequency regimes [35, 76–78]. Because physical dimensions of nanoantennas are typically on the order of the electromagnetic radiation

Figure 1: Emerging field of active plasmonics: The total number of citations to active plasmonics literature from 2004 to 2019 illustrates the remarkable growth in this field. (reference: Thomson Reuters Web of Science).

wavelength, PNAs are basically a nanoscale version of their much larger ubiquitous RF counterparts. Nevertheless, compared to RF antennas, PNAs operate based on distinct physical principles (Figure 2B) [35, 79]. Most importantly, nanoscale optical antennas offer extremely efficient energy conversion between localized electromagnetic fields and far-field optical radiation [35, 75, 76]. The fundamental mechanism behind this unique feature is the strong coupling of coherent free electron oscillations in metals (surface plasmons) to the continuum. At optical resonance, PNAs allow electromagnetic energy to be funneled from continuum to ultrasmall, nanometer-scale volumes through the excitation of LSPs, and vice versa. A variety of different PNA shapes and configurations support

LSPs, including triangular [51, 80, 81] and star-like geometries [82], core-shell structures [35, 83], miniaturized versions of Yagi-Uda antennas [84, 85], and V-shaped antennas [86, 87]. Independently from the PNA geometry, by virtue of coherent plasmonic excitations, incident electromagnetic energy is confined to the plasmonic antenna surface, leading to intense light focusing beyond the diffraction limit. Furthermore, PNAs have extinction cross-sections that are significantly larger than their physical cross-sections. This leads to remarkably efficient light focusing and gigantic field amplification (hotspots) [4, 88] (Figure 2C). By strongly enhancing local field intensities, PNAs can dramatically boost light-matter interactions by several orders of magnitude [13, 16].

Figure 2: Subwavelength plasmonic nanoantennas (PNAs): (A) A conventional dipolar antenna operating in the radio frequency (RF) regime. Connecting the antenna to an electrical coaxial wire enables highly efficient energy conversion between local RF sources and far-field electromagnetic radiation. Adapted from the study by Greffet [55]; (B) PNAs operating in the optical regime. Adapted from the study by Alù and Engheta [108]; (C) Electromagnetic energy is strongly focused through the optically resonant metal PNA when the localized surface plasmon resonance (LSPR) condition is met. Adapted from Brongersma et al. [88]; (D) Dielectric permittivity (experimental data by Johnson and Christy [109]) of gold at optical frequencies; (E) A schematic illustration of surface plasmon decay mechanisms: the plasmon can either decay radiatively through reemitted photons (left) or nonradiatively decay into energetic electrons (right). Adapted from the study by Clavero [110].

PNAs, due to their drastically enhanced optical scattering and extinction cross-sections at resonance, have become an indispensable tool in a plethora of cutting-edge applications, including single-molecule superresolution microscopy [50, 51], high-efficiency photovoltaics [12, 14], ultrafast quantum information processing [57, 89], ultra-sensitive biosensing [19, 22], integrated optical nanocircuitry [79], augmented reality [90, 91]. The latest advances in nanoscale fabrication and nanophotonic characterization techniques, as well as powerful electromagnetic simulation methods, have enabled scientists and engineers to understand and harness plasmonic excitations in metallic PNAs with high efficiencies [14, 31, 75, 76]. By employing these well-established toolsets, sophisticated devices can be readily designed with desired functionality through rigorous parametric optimization techniques [92, 93]. For example, a well-engineered array of PNAs can support long-lived and high quality (Q)-factor optical resonances and high field enhancements over a broad spectral range down to deep UV regime. One fascinating advantage benefiting from these nanostructures is the subwavelength interfacing of optics and electronics with superior response time and bandwidth over state-of-the-art optoelectronic systems [76, 81, 94].

2.1 High Q -factor broadband plasmonic nanoantennas

Optical characteristics of PNAs critically depend on the dielectric constants of the metal, an intrinsic property of the selected element (Figure 2D). Over the past decades, various materials have been explored [76, 95–100]. To date, gold (Au), silver (Ag), and aluminum (Al) remain the most commonly used metals for plasmonics because of their high free-electron density and low intrinsic losses [76]. However, to fully exploit strong light–matter interactions for practical purposes, considerable efforts have yet to be made to control plasmon damping processes in realization of high-quality factor (Q -factor) plasmon resonances [22, 92, 93, 101, 102]. Metallic resonators, such as PNAs, yield broad linewidth resonances due to rapid dephasing of coherent oscillations within 2–10 fs [101, 103]. Relatively short lifetimes of LSPs arise from plasmon damping through two dissipation channels: radiative decay (photon emission) and nonradiative losses (heat generation) [93, 101] (Figure 2E). Radiative losses are reversible and can be harnessed to excite neighboring plasmonic resonators [22, 104]. Nonradiative decay, however, leads to irreversible loss of electromagnetic energy [88, 105, 106]. Nonradiative decay is typically controlled by direct interband and

phonon-assisted intraband transitions, and Landau damping rates [93, 107]. At high optical frequencies, interband transitions, an intrinsic property of the metals, become particularly strong, precluding access to much of the UV and visible (vis) spectrum. Furthermore, rapid depletion of plasmon energy severely limits the buildup of optical near-field intensities, resulting in weaker light–matter interactions. It is of crucial importance to extend the lifetime of plasmonic excitations in order to realize strong electron–photon coupling and obtain high Q -factor LSPRs. Controlling radiative and nonradiative losses in metallic optical resonators, on the other hand, is a major challenge from both fundamental and practical perspectives.

Far-field coherent interactions in PNAs can lead to resonance linewidth narrowing due to partial cancellation of radiative losses when scattered photons from nanoantennas are recollected and harvested by their neighbors [104, 111–117]. Recent studies have shown that narrower resonances due to far-field coupled antennas provide particular advantages for practical applications [22, 118, 119]. Detailed information on far-field coupled nanoantenna arrays can be found in a recently published review article [120]. Studies on far-field coupled antennas have been mainly focused on red and near-infrared frequencies. We recently showed that long-lived plasmonic excitations can be realized over the entire visible spectrum and deep into the UV regime by quenching radiative losses. For this, we used far-field coherent interactions in Al nanoantenna arrays and harnessed distinctively favorable dielectric characteristics of the aluminum. Radiative losses dominate spectral broadening of the plasmonic resonances in Al nanostructures for the wavelengths below 800 nm. Hence, quenching of radiative damping is particularly effective in realization of pronounced line width narrowing within the green-blue-violet visible and near-UV regime. To minimize radiative losses, we introduced an elegant and universal approach enabling rapid and efficient inverse engineering of remarkably narrow linewidth and high Q -factor PNAs [92]. Our powerful and versatile inverse-design technique enables optimization of radiatively coupled PNA arrays fabricated on refractive index mismatched super-/substrates (Figure 3A). Traditional trial-and-error-based design approaches often require computationally expensive and time-consuming three-dimensional rigorous electromagnetic simulations of tens to hundreds of candidate structures [121, 122]. In contrast, we showed that our space mapping–based inverse design technique enables ultrafast and accurate retrieval of the fittest sets of structural PNA parameters, yielding the desired optical characteristics with a minimal number of high-fidelity and computationally expensive simulations [92]. Our inverse design approach establishes a

one-to-one mapping scheme [123, 124] enabling effective approximation of time-consuming finite difference time domain (FDTD) simulations using an analytical coupled dipole approximation (CDA) model that is not resource hungry. Using a parameter extraction approach, our coarse CDA model that rapidly finds and evaluates potentially promising candidate PNA structures is iteratively updated and calibrated against the fine FDTD model until the predefined convergence criterion is met, yielding the optimal structural design parameters. Typically, only a few rigorous FDTD simulations of the candidate PNA structures are needed since the fine model is only executed once in each iteration, as opposed to solving tens to hundreds of different candidate structures using a conventional trial-and-error strategy. Using this novel inverse design approach, we demonstrated remarkably high Q -factor ($27 \leq Q \leq 53$) Al nanoantenna arrays over the entire visible spectrum, outperforming even similarly optimized far-field coupled Ag nanoantenna arrays at the green-blue-violet wavelengths (≤ 550 nm) and in the near-UV regime (~ 300 nm) (Figure 3B). Subsequently, we demonstrated drastically narrow linewidth (~ 15 nm) and record high Q -factor ($Q \sim 27$) Al PNAs (Figure 3C), surpassing even the resonance characteristics of Al nanostructures relying on multipolar dark modes [125] and hybridized dipolar and quadrupolar modes [102].

2.2 High-throughput and scalable nanofabrication

Real-world adaptation of nanoscale technologies critically depends on the development of high-throughput and high-

yield nanofabrication techniques, offering structural uniformity at nanoscale over large areas. During the last few decades, we have witnessed remarkable advancements in high-throughput nanofabrication techniques based on top-down electron-beam [126], ion-beam [127], nanostencil [26, 128], nanosphere [129, 130] lithography and bottom-up self-assembly schemes [53, 82, 131–134]. However, major hurdles still remain in realization of large-scale, low-cost manufacturing of PNAs with minimal structural inhomogeneities and nonuniformities (polydispersity). As LSPR energy strongly depends on the feature sizes and geometries of PNAs, poorly controlled nanofeatures give rise to unpredictable LSPR behavior and unfavorable heterogeneous broadening of resonance linewidths, especially for small size nanoantennas [92, 93]. Fabrication of plasmonic nanostructures often requires metal lift-off processes, which can lead to significant variations in nanoscale features. Recently, we have demonstrated an effective strategy in tackling these challenges by employing a high-throughput wafer-scale lift-off free fabrication approach based on UV interference lithography and reactive ion etching [92] (Figure 4A). We demonstrated low-cost large-area nanofabrication of Al nanodisk arrays fabricated over 8-inch fused silica wafers with excellent structural uniformity with sub-30 nm feature sizes (Figure 4B–C). Employing this novel nanofabrication technique, we recently demonstrated remarkably high Q -factor Al nanoantenna arrays [92].

Nanostencil lithography (NSL), an alternative lift-off free fabrication technique, offers high-resolution nanofabrication capability on unconventional and flexible substrates [26, 128]. A major drawback of this technique, however, is the difficulty of fabricating large area

Figure 3: High Q -factor Al PNAs over a broad spectral window: (A) Space mapping algorithm enabling the inverse design of high Q -factor (narrow resonance linewidth) PNAs at the desired wavelength is shown; (B) Optical characteristics of coupled Al PNAs (blue color) and Ag PNAs (red color) that are designed using this space mapping algorithm are compared over a broad spectral range; (C) Experimentally measured extinction spectrum of optimized Al PNAs (red circles) demonstrates strong Fano-like resonance behavior (blue curve). Inset shows the cross-sectional near-field intensity profiles of the Al-PNAs. Adapted from the study by Zhu et al. [92]. PNA, plasmonic nano-antenna.

Figure 4: High-throughput and wafer-scale fabrication of PNAs: (A) Schematic of the DUV nanofabrication approach enabling lift-off free patterning of plasmonic nanostructures with exceptional uniformity. Adapted from the study by Zhu et al. [92]; (B) A (1 × 3 inch) glass slide with millions of Al PNA structures on it is shown; (C) Scanning electron microscope (SEM) image of Al PNAs fabricated on a glass substrate using this technique. Adapted from the study by Zhu et al. [92]; (D) Schematic illustration of the DUV-based nanostencil patterning technique enabling fabrication of PNAs in a lift-off free manner. High-quality and large-area nanostencils, free-standing silicon nitride (Si₃N₄) thin films with an array of open-ended nanoapertures, are first fabricated using the DUV nanopatterning. Adapted from the study by Zhu et al. [135]; (E) SEM image of a nanostencil with a periodic array of circular nanoapertures arranged in a square lattice. The nanohole diameter and array periodicity are 130 nm and 380 nm, respectively; (F) SEM image of an Au PNA array fabricated on a glass substrate using this nanostencil and mask deposition process. The diameter and height of the resulting nanodisk antennas are 140 nm and 120 nm, respectively. PNA, plasmonic nanoantenna; DUV, deep-UV; UV, ultraviolet.

nanostencil masks using electron-beam lithography. Recently, we adapted a deep-UV (DUV) lithographic nanofabrication technique enabling high-throughput wafer-scale manufacturing of large area stencils using suspended silicon nitride (Si₃N₄) membranes [135]. Using this technique, we demonstrated 4-inch wafer stencils housing 200 million nanoapertures with remarkably uniform nanoscale features. We used DUV-based NSL to pattern PNAs, i.e., nanodisk arrays, on a nonconductive glass substrate (Figure 4D). To do this, we placed nanostencils with open-ended nanoapertures in intimate contact with the substrate to ensure accurate transfer of the nanoantenna pattern with minimal shadowing effect (Figure 4E). Using a single directional metal deposition step, we demonstrated remarkably precise and reliable fabrication of 200 million Au nanodisk antennas on glass substrates (Figure 4F). Beyond the particular example shown here, this DUV nanofabrication scheme allows high-throughput fabrication of high-density PNAs on unconventional substrates, including rigid, flexible, stretchable, and biocompatible materials [26, 128].

2.3 Lumped optical nanocircuit theory

Adaptation of antenna concepts from the RF communications has revolutionized our ability to manipulate light at the subwavelength scale, opening up the possibility of merging electronics and photonics at nanoscale dimensions [79, 136, 137]. Likewise, concepts of lumped circuit elements and RF design provide guidelines for new technological advancements in nanoscale optics. Lumped circuit elements allow simplification of the analysis of complex circuits and enable conceptual understanding of each circuit element through effective modularization [138]. In this respect, a comprehensive understanding of the internal mechanism of each circuit element is not needed when designing a circuit; only the relation between the voltage across each element and the current flowing through it is sufficient. Therefore, by hiding much of the internal operational complexity within an individual device design, RF electronic circuits can be readily constructed with desired functionalities at the system level [16, 77, 136]. However, simple scaling of RF design concepts to

Figure 5: Optical nanocircuits: (A) The concept of optical nanocircuit theory in the optical domain. Adapted from the study by Engheta et al. [137]; (B) Lumped optical circuit element equivalents of materials with different dielectric permittivities. Nanocapacitor (top), nanoinductor (middle), and nanoresistor (bottom) are shown. Adapted from the study by Engheta [136]; (C) Schematic showing the equivalent optical circuit model of a loaded PNA (first and second panels). The far-field scattering spectrum of the PNA obtained with the optical nanocircuit model (third panel) is in remarkable agreement with the experimental measurements (fourth panel). Adapted from the study by Liu et al. [147]. PNA, plasmonic nanoantenna.

optical frequencies is not feasible. This is because at infrared (IR) and optical frequencies, metals suffer from strong Drude losses and do not exhibit conductivity in the conventional sense [136]. Therefore, a modified quantitative design approach, an analog of RF circuits, is needed.

Engheta [136] and Engheta et al. [137] pioneered a general theoretical framework for PNA-based optical nanocircuits using RF design concepts (Figure 5A). In their optical nanocircuit approach, metals ($\text{Re}[\epsilon] < 0$), insulators (the surrounding dielectric, $\text{Re}[\epsilon] > 0$), and losses are modeled as nanoscale capacitors, inductors, and resistors, respectively (Figure 5B). These three basic nanocircuit elements operating at the IR and optical frequencies form the basic building blocks and modules in designing “metatronic” circuits of arbitrary complexity. In their follow-up studies, Alù and Engheta [108, 139] further developed the concepts of optical input impedance, optical radiation resistance, loading, and impedance matching in the optical

frequency regime. By solving Maxwell’s equations and Kirchhoff’s current law, electric field and “flowing optical current” are tightly linked to the optical impedances of lumped nanocircuit elements, in the same way one would model the electric current flowing in an RF lumped circuit.

Based on Alù and Engheta’s groundbreaking work [137], significant progress has been made by many other research groups [10, 140–151] in demonstrating novel uses of plasmonic devices with functionalities merging electronic/electrochemical/mechanical phenomena with optics at the nanoscale. Based on lumped optical nanocircuit theory, researchers demonstrated design, optimization, and analysis of novel practical PNA-based devices and realized plasmonic nano-optic devices that work seamlessly in the optical domain [10, 139, 147]. One of the most notable examples is the impedance-matched optical dimer nanoantennas designed using fully three-dimensional (3D) lumped nanocircuit models [147] (Figure 5C). In this work,

Liu et al. used lumped circuit elements to realize accurate control and tuning of PNA optical response with great flexibility [147]. Authors employed a retrieval method [145] to determine the inductance, capacitance, and resistance values of the nanoantenna by conducting full-wave numerical simulations of the nanoantenna driven by a discrete current source. They demonstrated a nanocircuit approach to construct PNA-based optical nanofilters with various topologies, opening the door to the development of integrated optical circuits for applications in data storage and wireless optical links.

3 Reconfigurable plasmonic nanoantenna

Conventionally, optical resonance characteristics of PNAs are set during the design/fabrication process and can only be altered with permanent morphological changes [152]. The need for reversible reconfigurability in plasmonic response has spurred broad research activities during the past two decades. A concerted and interdisciplinary effort has been devoted to the development of active systems in realization of postfabrication dynamic reconfigurability in a fully reversible and repeatable, fast, and ideally programmable manner. Until now, a variety of schemes have been proposed and developed in pursuit of *in situ* active control by electrical [153–155], chemical [156–159], optical [160], thermal [161], or mechanical [162–164] means. A key aspect of active PNAs is the scalability and reconfigurability through precise control over structural dimensions, material transitions, surrounding media, and near-field couplings among individual components in the case of multielement arrangements. From a practical perspective, active PNAs with tunable resonances enable critical optical functions needed for ultrabroadband sensors [165], tunable flat lenses [166], holograms [167], dynamic switches [66], interferometry photonic platforms [168], neural activity tracking [10, 69], and information encryption [169]. Physical mechanisms behind these active plasmonic devices can be understood using lumped optical nanocircuit theory. In the following sections, we show that there are three distinct routes enabling dynamic reconfigurability in PNA devices (Figure 6). The first approach is based on direct modulation of the dielectric properties of the metal, which is effectively equivalent to tuning of the nanoantenna inductance (Figure 6A). The second approach is the controlled loading of PNAs with active materials, which can be interpreted as tunable nanoinductors or nanocapacitors within the lumped optical nanocircuit

(Figure 6B). The third approach relies on modulation of the near-field coupling between adjacent nanoantenna elements in a multielement PNA arrangement. In such devices, variations in the coupling strength can be described using a tunable nanocapacitor that bridges different nanocircuits representing different nanoantenna elements (Figure 6C). These active PNA approaches are developed for different specific applications and have their own strengths and limitations as listed in Table 1.

3.1 Modulation through metallic properties

The first approach is through active tuning of PNA inductance (Figure 6A). This can be achieved by direct modulation of the free carrier densities and dielectric functions of the conductive metal nanostructures by means of crystalline phase transitions or electrical gating. The frequency-dependent permittivity of metals can be described by the Drude model [30] as follows:

$$\begin{aligned}\varepsilon_{\text{metal}}(\omega) &= \varepsilon_r(\omega) + i\varepsilon_i(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\omega\Gamma} + \varepsilon_{\text{inter}}(\omega), \\ \omega_p &= \sqrt{\frac{n_e e^2}{m^* \varepsilon_0}}\end{aligned}\quad (1)$$

where ε_r and ε_i are the real and imaginary parts of the dielectric function, ε_∞ is the high-frequency-limit dielectric constant, ω is the frequency of light, Γ is the damping frequency, $\varepsilon_{\text{inter}}$ represents the contributions of interband transitions, and ω_p is the plasma frequency. Plasma frequency depends on the carrier density n_e , electron charge e , and effective mass m^* . In the quasi-static regime (nanoantenna diameter $d \ll$ wavelength of light λ) [30], the Fröhlich condition, corresponding to LSPR in a Drude free-electron metal nanoantenna, is fulfilled when $\varepsilon_r = -2$. LSPR occurs at $\omega_f \approx \omega_p/\sqrt{3}$, where ω_f is the Fröhlich frequency. Hence, LSPR frequency is controlled by the electron density at the Fermi level, as in $n_e(\omega_f \sim \sqrt{n_e})$.

3.1.1 Crystalline phase transition

Catalytically active noncoinage transition metals, such as metal hydrides, have emerged as a particularly promising class of materials for active nanoplasmonics (Figure 7A). These materials typically undergo *in situ*, reversible crystalline phase transformations between metallic and dielectric hydride states through hydrogenation and dehydrogenation (Figure 7B). The resultant crystal and electronic band structure alterations lead to drastic changes in the optical properties of PNAs, thereby

Figure 6: Mechanisms employed for active PNAs with the corresponding lumped optical nanocircuit equivalents: (A) Modulations in the optical dielectric constants of a PNA metal are captured using tunable nanoinductors; (B) Modulation of PNA characteristics through the coupled dielectric medium is incorporated using a tunable load consisting of nanocapacitors or nanoinductors; (C) Modulation of the near-field coupling between PNA elements is represented by tunable nanocapacitors. (A)–(C) The left panel shows the lumped optical nanocircuit representation of active PNAs for various tuning mechanisms. The right panel illustrates reversible tuning of PNA response through material characteristics based on different physical phenomena. PNA, plasmonic nanoantenna. r , radiative; nr , nonradiative.

causing remarkably strong LSPR modulations. Metal hydrides have attracted significant interest in realization of optical hydrogen sensors [180–182], switchable mirrors [183, 184], chirality switching [185], and dynamic color displays [169]. Palladium (Pd), magnesium (Mg), zirconium (Zr), titanium (Ti), and vanadium (V) are some of the most studied metal hydride materials. Mg, in particular, has attracted a great deal of attention [74] due to its earth abundance, low cost, reversibility, and superior plasmonic properties at high optical frequencies.

Furthermore, it offers excellent gravimetric and volumetric hydrogen storage capacities [186] and benefits from the high surface-to-volume ratios offered by this material. Mg-based PNAs with remarkably fast diffusion kinetics have been shown [187]. Recently, there is growing interest in metal alloy (e.g., Mg–Pd, Au–Pd) PNAs to realize broader dynamic tuning range and faster response times. Another focus is to suppress the unfavorable hysteresis effect during the de-/hydrogenation processes with respect to single-metal-based devices

Table 1: Comparison of three mechanisms employed for active PNA tuning.

Mechanisms	Strengths	Limitations	References
A. Modulation of PNA metallic properties			
Electrical gating	(i) Excellent reversibility; (ii) Stable, no electrochemical degradation	(i) Small electric field sensitivity (0.00028 nm/mV); (ii) Small LSPR shift (<2.5 nm); (iii) Small SSNR (<0.09)	[10, 170]
Crystalline phase transition	(i) Large LSPR shift (>50 nm)	(i) Slow switching time (minutes); (ii) Nonlocalized	[171]
B. Modulation via loading			
<i>Capacitive loading</i>			
Loading in bulk medium	(i) Large LSPR shift (~192 nm); (ii) Small gating voltage (~1 V)	(i) Instability due to photobleaching; (ii) Slow switching time (seconds); (iii) Limited tuning range	[172–175]
Nanoscale loading	(i) High electric field sensitivity (0.91 nm/mV); (ii) High SSNR (>200); (iii) Fast response (~200 μ s); (iv) Low energy consumption (9 fJ/pixel); (v) Excellent reversibility	(i) Limited tuning range; (ii) Electrochemical degradation	[10, 71, 160]
<i>Inductive loading</i>			
Graphene nanoload	(i) Large LSPR shift (>650 nm); (ii) Excellent reversibility	(i) Limited to NIR and MIR wavelengths; (ii) Large gating voltage (>10 V)	[176]
Metal nanoload	(iii) Large optical contrast (~80%)	(iii) Limited reversibility (~30 cycles); (iv) Electrochemical degradation; (v) Complicated nanofabrication	[73, 177]
C. Modulation via near-field coupling			
	(i) Low energy consumption; (ii) Large LSPR shift (>100 nm); (iii) Excellent reversibility	(i) Small SSNR; (ii) Sophisticated optical setup	[163, 178, 179]

PNA, plasmonic nanoantenna; LSPR, localized surface plasmon resonance; SSNR, signal-to-shot-noise ratio; NIR, near-infrared; MIR, mid-infrared.

[74, 182] (Figure 7C). More information on metal hydride-based PNAs can be found in recent reviews [74, 188].

3.1.2 Electrical gating

Field-effect tuning of the free-carrier density of metals offers a reversible modulation capability of the PNA spectral behavior at high speeds [189–191]. Modulation of the plasmonic response of a PNA via an externally applied bias can be accomplished in either dielectric media [10, 69] or ionic solutions [192, 193]. In a typical dielectric medium such as air, an external field can modulate plasmonic resonances by changing the carrier density n_e of the PNA within a skin depth at the surface, known as Thomas–Fermi screening length [157, 194, 195]. Depending on the direction of the applied electric field, carrier density Δn_e increases (decreases) due to charge accumulation (depletion) at the surface [196, 197]. This free-carrier density variation results in alteration of the plasma frequency ω_p . According to the Drude model, changing electron density

leads to modulation of the metal permittivity, causing spectral shifting of the LSPR [198].

Compared to electrical biasing in a dielectric medium, electrical gating within an ionic medium (i.e., liquid- or solid-state electrolyte solution) can lead to stronger LSPR modulations [199, 200]. Plasmonic response in ionic media can be tuned through non-Faradaic [201, 202] and Faradaic [203–205] charging effects. In non-Faradaic processes, application of an electrical potential difference between a PNA and a reference electrode results in the formation of an atomic scale ($\sim \text{\AA}$) electrical double layer (EDL) on the nanostructure surface. This EDL consists of an internal Stern and an adjacent Gouy–Chapman diffuse layers (Figure 8A). The Stern layer is formed by specific adsorption of counterions, while the diffuse layer emerges due to the nonspecifically adsorbed ions that screen the charges on the PNA surface. Strong electric field within the EDL results in alteration of the plasma frequency ω_p , leading to a spectral shift of the PNA resonance [199, 206, 207]. Using the Drude model and double-layer capacitor approximation, the modulation depth and speed of the plasmon

Figure 7: Crystalline phase transition: (A) *In situ* crystalline phase transformations. The top panels show schematics of PNAs consisting of metal and metal hydrides. The bottom panels display the complex dielectric function of each metal and its hydride. Adapted from the study by Palm et al. [188]; (B) Crystallographic phase transition between metal and metal hydride takes place during de-/hydrogenation processes. Inset shows the atomic arrangements in the Mg (0001) and MgH₂ (110) crystal planes. Adapted from the study by Duan and Liu [74]; (C) Suppression of the unfavorable hysteresis effect during de-/hydrogenation processes by using metal alloy PNAs. Top panel illustrates the nanofabrication of a metal alloy PNA using hole-mask colloidal lithography (left) and thermal annealing (right) methods. The bottom panel displays hydrogen adsorption and desorption isotherms for three different alloy compositions. Adapted from the study by Wadell et al. [182]. PNA, plasmonic nanoantenna.

Figure 8: Faradaic and non-Faradaic charging of PNAs: (A) Non-Faradaic charging results in redistribution of free-carrier charges in an atomic-scale electrical double layer surrounding the PNA; (B) Faradaic charging leads to injection or extraction of electrons through redox electrochemical reactions. PNA, plasmonic nanoantenna.

resonance can be determined [207, 208]. The resonance wavelength shift linearly scales with the applied potential, whereas the switching speed is dominated by the “RC” charging time of the EDL. A key demonstration of non-Faradaic charging effects was reported by Huang et al. [202, 206]. In their experiments, they demonstrated that the scattering efficiency of PNAs can be modulated through non-Faradaic charging processes using an external electrode. In addition, they showed that the surface plasmon modes of the PNAs with elongated morphologies (plate or rod shape) exhibited higher oscillator strengths and therefore were more sensitive to surface charge perturbations with respect to PNAs with spherical shapes [202].

Faradaic charging arises from electrochemical reactions that take place at the interface between PNAs and their surrounding electrolyte [158, 209–213]. This process involves electron transfer between the chemical species and the plasmonic nanostructures. In Faradaic electrochemical dis-/charging processes, a metallic nanoantenna is coupled to redox reactions (oxidation/reduction), acting as a reservoir for the electrons (Figure 8B). In cyclic redox reactions, electrons can be stored in the PNA material and donated back to the chemical species in an alternating manner. Electron transfer in and out of a plasmonic structure leads to cyclic spectral modulation (blue/red shifting) of its LSPR. So far, the Faradaic charging mechanisms have been employed to monitor the catalytic behavior [211, 214, 215], visualize photoinduced electrons [216], and observe the dynamics of electrochemical reactions [212, 217, 218]. Although both non-Faradaic and Faradaic charging methods enable precise control and reversible manipulation of the free-carrier density of PNAs, tunability is often limited due to the unpractically large external field requirements. Intrinsic free-carrier density ($n_e \sim 10^{23} \text{ cm}^{-3}$) of metals is often significantly higher than the modulation itself ($n_e \gg \Delta n_e$) at practical voltages. Therefore, alterations in metal plasma frequency are often small ($\Delta\omega_p = \Delta n_e (\omega_p/2n_e)$) [10]. One approach to mitigate this issue is to use low electron density metals such as indium tin oxide ($\sim 10^{20} \text{ cm}^{-3}$) [193]. However, low density metals offer LSPRs only at longer wavelengths, such as THz frequencies [193, 219].

3.2 Loading of plasmonic nanoantennas

One effective approach to achieve high tunability is to employ an external nanoscale load (Figure 6B). Modulations in the effective refractive index of the dielectric medium surrounding the PNA can be utilized to dynamically tune the peak position of the plasmonic resonance.

Because the local electromagnetic field extends beyond the physical boundaries of a PNA, the resonant characteristics of PNAs are extremely sensitive to the dielectric environment surrounding it. Active PNAs can be realized by modulating the complex dielectric function of the surrounding medium via an external mechanism (Figure 6B, right panel, first row). To date, the most promising active dielectric materials include liquid crystals [220–223], nonlinear materials [224–226], photochromic dyes [67, 172], amorphous–crystalline phase change materials [227–231], pH-sensitive polymers [232, 233], and electro-active materials [173, 234, 235]. These materials present effective refractive index modulation in response to external stimuli, such as pH and temperature change, incident light, and external electrical and magnetic field. Active control of PNA resonances can be achieved by controlling light–matter interactions within nanoscale volumes (plasmonic hot spot) near the antennas, which are typically much smaller than the volume of the bulk active medium (Figure 6B, right panel, second row). For some applications, such as multiplexed neural tracking with subcellular resolutions [10] and dynamic color displays [169], it is desirable to minimize the active media thickness conjugated to PNAs in order to attain high switching speeds between different resonant states.

In RF engineering, a dipolar loaded antenna consists of two half dipole antennas separated by a feed gap. The feed gap is often connected with an electronic circuit that can be readily tuned externally, which enables active modulation of the antenna response. In essence, tunable feed gap is an indispensable part of conventional RF antennas and provides a practical approach for dramatic enhancement of the “electrical length” (i.e., electrical resonance). Using lumped electronic circuit elements in the inter-antenna gap, broadband resonant antennas can be realized. From a fundamental perspective, the “electrical length” concept plays a crucial role in tuning and matching RF antenna resonances with a great degree of freedom and without physically altering the antenna’s length and/or shape. Inspired by the tunable conventional RF technology, researchers have designed plasmonic analogs – loaded PNAs (LD PNAs), which are composed of two tightly coupled nanoantenna arms separated by a narrow tunable gap at deep subwavelength scale [108, 139, 147]. This “slot region” is an analogue of the feed element in RF antennas [139, 236]. Inter-antenna feed gap load can be externally controlled, opening the door for active spectral tuning of the dipole antenna response (Figure 6B, right panel, third and fourth row). From the optical nanocircuit perspective, inserting nanoloads with tunable dielectric permittivities into the slot region leads to variations in the feed gap

capacitance/inductance. This results in alterations in the resonance frequency and far-field extinction spectrum of the antenna–load system. We want to emphasize that the framework of nanocircuit theory is the key to designing tunable LD PNA systems with desired functionalities. This is because the theory offers unambiguous physical insights into the general behavior of LD PNAs in response to external stimuli that give rise to modulations of the nanoload permittivities. Moreover, it provides clear guidelines in designing tunable LD PNAs with excellent modulation depths, low switching thresholds, and ultrafast time responses.

To date, researchers have harnessed strong light–matter interactions enabled by PNAs to create novel LD PNA configurations with varying degrees of sophistication. Beyond the traditional split nanodipole antenna layout [145, 237–239], LD PNAs have been designed in a sphere-, rod-, disc-, and dumbbell-shaped core–shell heterostructure [10, 160, 177, 240–242], heterodimer [73, 181, 243], composite trimer [244], molecular-level grafting [70, 245–247], and atomic-scale filamentary bridge [153, 176] configurations. In all these proposed nanoantenna configurations, the thickness of the nanoload is generally not larger than the electromagnetic field decay length of LD PNAs. Ultrathin nanoloads not only facilitate the exploitation of the strong light confinement and local field enhancement offered by PNAs but also permit efficient coupling of the

local physical mechanism to the external stimuli within the subwavelength feed gap volumes ($\sim \text{nm}^3$). Until now, a wide range of active materials, including photoconductive semiconductors (silicon) [237], graphene [176], conductive filament [153], metal (silver) [177], metal hydrides (e.g., Pd) [73, 243], conductive polymers [10, 160, 177, 240–242], and nonlinear optical materials [32], have been employed as tunable nanoloads (Figure 9). These nanoloads change their optical properties depending on external stimuli, such as pH and ionic strength change, light excitation, temperature variation, phase transition, electrical gating, and magnetic tuning [70, 242].

Antenna loading schemes can be classified into two distinct categories: capacitive and inductive nanoloading. Tuning of the capacitive nanocircuit load by electrical gating leads to a novel class of active plasmonic devices, such as electrochromic-plasmonic (electro-plasmonic) nanoantenna. In a recent publication, we harnessed the low free-carrier density property of a conductive polymer (poly(3,4-ethylenedioxythiophene): polystyrene sulfonate, PEDOT: PSS) to overcome the low inherent electric field sensitivity of pristine PNAs [10]. We demonstrated that non-Faradaic charging of the conductive polymer can lead to strong modulations in the far-field optical response of the LD PNAs (Figure 9A). Furthermore, we observed that the Faradaic charging of the polymer through redox reactions also leads to even more drastic shifts in the spectral

Figure 9: Active loading of PNAs: (A) Non-Faradaic modulation of PEDOT:PSS-load (red) enables strong electro-optic modulation of Au PNA resonances. Adapted from the study by Habib et al. [10]; (B) Local field enhancement (hot spot) of the LD PNA. Adapted from the study by Peng et al. [160]; (C) PANI-loaded PNA shows strong modulations in both resonance spectra and scattering intensity due to Faradaic charging processes. (left to right: oxidized to reduced PANI). Adapted from the study by Peng et al. [160]; (D) A LD PNA is created in an Au/Ag core–shell fashion. Ag is employed as an inductive nanoload. Reversible transitioning of the nanoparticle shell between Ag and AgCl enables active tuning of the optical resonances of the LD PNA. Adapted from the study by Byers et al. [177]; (E) Graphene, serving as an inductive nanoload, is inserted into the inter-antenna gap to create an LD PNA structure. Electrical

gating of graphene modulates its free-carrier density, leading to a change in the nanoload inductance and thereby alters the spectral resonance of the LD PNA. Adapted from the study by Yao et al. [176]; (F) Schematic showing an LD PNA that incorporates Pd as an inductive nanoload. Pd exhibit significant changes in its dielectric function during a reversible crystallographic phase transition process triggered by de-/hydrogenation. Adapted from the study by Liu et al. [73]. PNA, plasmonic nanoantenna; PEDOT:PSS, poly(3,4-ethylenedioxythiophene): polystyrene sulfonate; LD PNA, loaded PNA; PANI, polyaniline.

resonance of LD PNAs. Spectral shift was large enough to cause the scattered light to exhibit noticeable color differences. Faradaic charging effects in conductive polymers, are particularly promising for the development of plasmonic color displays [242, 248–250]. Another prominent example of capacitive nanoloading is reported in an earlier work [160]. Peng et al. constructed an LD PNA platform by incorporating a conductive polymer (polyaniline) as the nanoload [160]. They showed strong modulating capacity of the complex refractive index of this polymer on the LSPR of the LD PNA. Figure 9B shows the electric field profile of the nanoparticle-on-mirror system where an Au PNA is encapsulated within a polyaniline shell. They utilized unprecedented field localization (hot spots) in Au PNAs to enhance the spectral sensitivity to the alterations in the optical properties of the capacitive nanoload. In their demonstration, application of a negative potential results in donation of electrons to the electrochromic nanoload, leading to strong modulations in the far-field spectra. According to optical nanocircuit theory, the increased electron density through external field is effectively equivalent to a diminished nanoload capacitance. As a result, resonance frequency of the LD PNA decreases. They observed a strong red shift (>100 nm) in the plasmonic resonance spectra (Figure 9C). On the contrary, a reversal of the sign of the applied potential causing electrons to leave the nanoload lead to a strong blueshift of the antenna resonance (Figure 9C). Exploiting Faradaic charging effects, the scattered light from the LD PNA was shown to present a drastic color change, and a palette of different colors was successfully generated.

In the case of inductive loading, metals and two-dimensional materials are among the most promising candidates to realize effective tuning of the LD PNA systems. Byers et al. [177] used a metal as an inductive nanoload and demonstrated active plasmonic tuning of an Au/Ag core-shell PNA structure in a fully reversible fashion (Figure 9D). By implementing a well-established Ag–AgCl redox chemistry, they achieved drastic changes in the nanoload dielectric constants via Faradaic charging. This work provides a new direction for the development of layer-by-layer active PNA devices. In a separate study, Yao et al. [176] employed graphene as an inductive nanoload (Figure 9E). They achieved a broad tuning range of more than 650 nm in LSPR through electrical tuning of the graphene electron density [176]. Inductive nanoload tuning can also be achieved through chemical reactions. A prominent example of this has been shown in a recent work by Liu et al. [73], where the authors harnessed crystallographic phase transitions through a process of de-/hydrogenation to modulate the dielectric function of a metal/

metal hydride material (Figure 9F). In their LD PNA system, a Pd PNA, serving as the inductive nanoload, was placed in the near vicinity of an Au PNA. In this unique metal dimer configuration, these two PNAs were strongly coupled to each other through localized plasmonic excitations. Essentially, the spectral characteristic of the antenna ensemble strongly depends on the optical properties of the Pd PNA. When the Pd PNA undergoes a crystallographic phase transformation from metal to metal hydride upon de-/absorption of hydrogen at its interstitial site, a dramatic change in the Pd permittivity is observed. Tuning of this inductive nanoload through phase transitions leads to significant modulations in near-field couplings between the PNAs, thereby enabling far-field optical response to be effectively modulated.

3.3 Tuning of near-field coupling

Use of the mechanical degree of freedom offers an alternative way to dynamically modulate plasmon modes of the nanoplasmonic structures. In a coupled multielement system, strong near-field interactions among individual components control the resonance behavior. In principle, physical distances between the elements modulate their coupling strengths and the far-field response of the entire system. This type of dynamic modulation can be understood within the framework of optical nanocircuit theory (Figure 6C). So far, there are three distinctively different approaches that have been developed to achieve dynamic tuning of the plasmon coupling strength between closely spaced nanoantenna structures. The first approach involves lithographically fabricated PNAs on a mechanically tunable elastomeric substrate [163, 164, 166, 251, 252]. By applying high-strain mechanical deformation (stretching/relaxation) to the compliant substrate, distances between resonant nanoantennas are modulated with nanometer precision (Figure 10A). Researchers achieved a spectral tuning range of more than 100 nm in a reversible and programmable manner. The second approach uses PNAs that are fabricated on a stiff pillar substrate. Pillars can be deformed when illuminated by high-energy electrons [178], strongly coupling the intrinsic mechanical and electromagnetic degrees of freedom. By taking advantage of the in-gap plasmonic modes, researchers have demonstrated a remarkably precise tuning capability with electron beam illumination (Figure 10B). The third approach utilizes coupled PNAs that are fabricated using a bottom-up self-assembly technique. PNAs are coupled to each other using molecular structures with a conformational degree of freedom. Researchers demonstrated dynamically

Figure 10: Tunable near-field plasmon coupling: (A) Optical response of PNAs fabricated on a stretchable soft substrate can be reversibly tuned by strain modulation. Adapted from the study by Yang et al. [163]; (B) Inter-antenna gap of a pillar-bowtie PNA can be tuned under electron beam illumination to realize active devices. Scale bars, 50 nm. Adapted from the study by Roxworthy et al. [178]; (C) An illustration of possible ways for dynamic reconfiguration of DNA-based PNAs. Adapted from the study by Zhou et al. [179]. PNA, plasmonic nano-antenna.

Figure 11: Scaling of microelectrode arrays (MEAs): (A) A timeline of transistor (top panel) and MEA recording (bottom panel) technologies over the past five decades. The MEA images are adapted from the studies by Thomas et al. [259], Connolly et al. [260], and Tsai et al. [261]. The CPU images are adapted from the courtesy of 'Wikimedia Commons' and 'AMD'; (B) MEA comparison in terms of electrode density and total sensing area. Adapted from the study by Obien et al. [262].

reconfigurable plasmonic nanostructures in a programmable manner by selectively manipulating relative PNA alignment via external stimuli such as pH and light [179, 253] (Figure 10C).

4 Electro-plasmonic nanoantenna and electrophysiology

One of the most exciting and promising applications for electro-active PNAs is the wireless measurement of electrophysiological signals. Electrophysiological measurements are routinely employed to understand electrical activity of cells linking low-level electrogenic circuits to high-level organ functions (e.g., memory and metabolism) [254]. Mapping electrophysiological signals is critically important for advancements in neuroscience, cardiology, and cellular biology at levels ranging from the molecular and cellular to the behavioral level. In this respect, development of electrophysiological recording techniques has created tremendous interest [254–256]. Since Luigi Galvani's groundbreaking discovery on the electrical nature of neurophysiology in the late 1770s, immense effort has been invested in developing electrophysiological tools capable of measuring bioelectric

activity of excitable cells [257, 258]. Despite considerable progress made over the past century, no existing technology offers simultaneous electrophysiological recordings from large networks of electrogenic cells with high spatiotemporal resolution.

To date, the most reliable electrophysiological recording tools are micrometer size multielectrode arrays (MEAs) [262–264] (Figure 11A). In principle, MEAs can record local field potentials in the extracellular space induced by transmembrane ion movement during cell firing events [265, 266]. However, use of electrons as information carriers imposes several fundamental constraints due to the electronic nature of the measurements. In MEA measurements, every recording site or electrode in the array either has to be wired to an external signal processing unit or requires on-chip conditioning [262]. Shrinking the overall footprint of the metal electrodes, although offers markedly increased multiplexity and density of individually addressable recording channels, adds a high level of complexity in electrical circuitry and wiring (Figure 11B). Furthermore, reducing electrode sizes inevitably introduces unwanted interchannel cross-talk and results in increased electrode impedance and thermal noise, degrading the signal-to-noise ratio [267]. This density versus noise tradeoff severely restricts the accessibility to desired multiplexing and bandwidth operation capabilities for simultaneous

Figure 12: Electro-plasmonic nanoantenna enabling label-free electrophysiological recordings optically: (A) False-color SEM image showing a cardiomyocyte cell cultured on a large array of electro-plasmonic nanoantennas; (B) SEM image showing selective deposition of PEDOT:PSS on Au PNAs. The polymer is conformally coated on each nanoantenna structure using a selective electropolymerization scheme and employed as a capacitive nanoad. (C) Local electric field enhancement within close proximity the electro-plasmonic nanoantenna (top view); (D) The far-field scattering spectrum of the electro-plasmonic nanoantennas is acquired using a spectroelectrochemical dark-field transmission measurement setup; (E) Electro-plasmonic nanoantennas allow label-free, real-time, and remote optical detection of the local electrogenic activity of the cardiomyocyte cells (red curve). No dynamic far-field scattering signal is detected in the absence of electro-plasmonic nanoantennas (blue curve). (A)–(E) are adapted from the study by Habib et al. [10].

PEDOT:PSS, poly(3,4-

ethylenedioxythiophene):polystyrene sulfonate; SEM, scanning electron microscope; PNA, plasmonic nanoantenna.

recording of a large number of electrogenic cells. Well-established semiconductor industry manufacturing capabilities allow recording electrodes to be reduced in size and integrated with high density using complementary metal-oxide-semiconductor (CMOS) technology. However, implementing extremely small metal electrodes poses an enormous challenge due to parallel interfacing requirements imposed by relatively sizable peripheral recording electronics that secure the connections between multiplexed inputs and outputs [261, 267, 268]. Due to this fundamental bottleneck, multiplexed measurement capabilities of MEAs have been limited [267].

Unlike microelectrode recordings, use of photons offers unparalleled (time/wavelength division) billion-fold enhanced multiplexing and information carrying capabilities. Photons are extremely fast and do not interact with each other. In principle, one can use photonic elements to realize high-bandwidth electrophysiological recordings without on-chip conditioning. Achieving this goal, however, largely depends on our ability to recruit reliable electro-optic translators that can efficiently convert bioelectric signals to high photon count optical signals [254]. This necessitates development of new photonic systems with excellent electro-optic characteristics.

We recently introduced an ultrasensitive and extremely bright nanoscale electric field probe enabling wireless monitoring of the electrophysiological activity of cells with light [10]. Using massively multiplexed electro-PNAs, we demonstrated reliable detection of local electric field dynamics with remarkably high signal-to-shot-noise ratios from diffraction-limited spots (Figure 12A). We showed that low-frequency (1 kHz) cell spiking signals can be remotely monitored using high-frequency (~ 460 THz) electromagnetic radiation. Our novel optical field-probing approach is based on tunable RF circuit concepts. Here, the electro-PNA, consisting of a metallic nanoantenna structure encapsulated in a tunable biocompatible electrochromic polymer matrix, is reminiscent of an ordinary radio antenna connected to a tunable load circuit (Figure 12B). In this unique electro-plasmonic system, alteration of the electrical and dielectric properties of the polymer in response to local electric field oscillations leads to active and reversible tuning of the far-field optical response of the nanoantenna. We exploited extreme light confinement and gigantic local field enhancement properties of the electro-PNAs to drastically boost light-matter interactions and enhance detection sensitivity of the local electric field dynamics with a sub-millisecond (< 0.2 ms) temporal resolution (Figure 12C). We demonstrated large scattering intensity changes up to 7% for low field values of 8×10^{-2} mV/nm, which is consistent with electrophysiological measurement requirements

(Figure 9A); ionic movements of sodium (Na^+) and potassium (K^+) typically lead to a strong electrical field modulations on the order of 10^{-2} – 10^{-1} mV/nm [269]. We achieved more than 3000-fold enhanced field sensitivities over pristine PNAs [69]. By tracing the resonance wavelength of the electro-PNAs through transmission dark-field measurements (Figure 12D), we demonstrated real-time, label-free detection of the bioelectric activity of cardiac cells using remarkably low-intensity light (~ 11 mW/mm²) (Figure 12E).

5 Conclusion

In conclusion, we reviewed recent developments in active plasmonics and various strategies for rational design of tunable PNAs for a myriad of emerging applications, including nanoscale gas sensing, dynamic color displays, and electrophysiological recordings. We first discussed general properties of PNAs, inverse design, high-throughput and ultraprecise nanofabrication, and an intuitive optical nanocircuit theory capturing the sophisticated spectral characteristics of active PNAs. We then discussed how to create dynamically reconfigurable PNAs using the bulk material properties (free-carrier densities, electronic structures), loading PNAs with suitably tailorable materials or conjugating them with flexible structures. In particular, we exploited the well-established lumped optical nanocircuit theory to categorize commonly adopted active tuning strategies dictating dynamic reconfigurability. We showed that optical nanocircuit theory provides unambiguous insights and guidelines in the ensuing development and studies of future active PNAs with desired optical functionalities. We finally presented the use of active PNAs for wireless and large-scale electrophysiological recordings of the electrophysiological activity of cells.

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