

# Optoelectronic Synapses Based on Hot-Electron-Induced Chemical Processes

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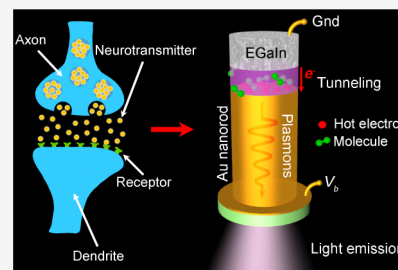
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**ABSTRACT:** Highly efficient information processing in the brain is based on processing and memory components called synapses, whose output is dependent on the history of the signals passed through them. Here, we have developed an artificial synapse with both electrical and optical memory effects using chemical transformations in plasmonic tunnel junctions. In an electronic implementation, the electrons tunneled into plasmonic nanorods under a low bias voltage are harvested to write information into the tunnel junctions via hot-electron-mediated chemical reactions with the environment. In an optical realization, the information can be written by an external light illumination to excite hot electrons in the plasmonic nanorods. The stored information is nonvolatile and can be read either electrically or optically by measuring the resistance or inelastic-tunneling-induced light emission, respectively. The described architecture provides a high density ( $\sim 10^{10} \text{ cm}^{-2}$ ) of memristive optoelectronic devices which can be used as multilevel nonvolatile memory, logic units, or artificial synapses in future electronic, optoelectronic, and artificial neural networks.

**KEYWORDS:** Artificial synapse, plasmonic tunnel junction, hot electrons, memristor



Highly efficient information processing in the brain utilizes multilevel (as opposed to binary used in modern digital computers) electrochemical logic components called synapses, which do not consume energy (nonvolatile) while in a passive state. A memristive device (or memristor) is a resistive electrical element with resistance depending on the history of the applied electrical signals.<sup>1,2</sup> It can be used as a memory element for the storage of information or as an artificial synapse to emulate biological synapses in spiking neural networks (SNNs) as well as nonspiking artificial neural networks (ANNs).<sup>3</sup> Since the first experimental realization based on a metal/oxide/metal (Pt/TiO<sub>2</sub>/Pt) structure,<sup>2</sup> memristors have attracted extensive interest due to their important applications in next-generation nonvolatile memory, signal processing, reconfigurable logic devices, and neuromorphic computing.<sup>4–17</sup> Most of them rely on a dynamically configurable insulating layer under applied electric bias. To date, memristor realizations are typically based on two approaches relying on (i) filament formation or annihilation upon control bias application in the insulating layers<sup>7,14,16</sup> and (ii) spintronic devices based on magnetic tunnel junctions where the spin-polarized current leads to the movement of the magnetic domain walls.<sup>5,12,13,15</sup> In both realizations, the flowing current leads to the changes of the device resistance; however, in order to reverse the effect, a bias of opposite polarity needs to be applied. By integrating light-emitting or plasmonic properties with memristive devices, memristors with an optical read-out have also been demonstrated (still requiring electric bias for changing the memristor state),<sup>9,18–23</sup> which are attractive for applications in optoelec-

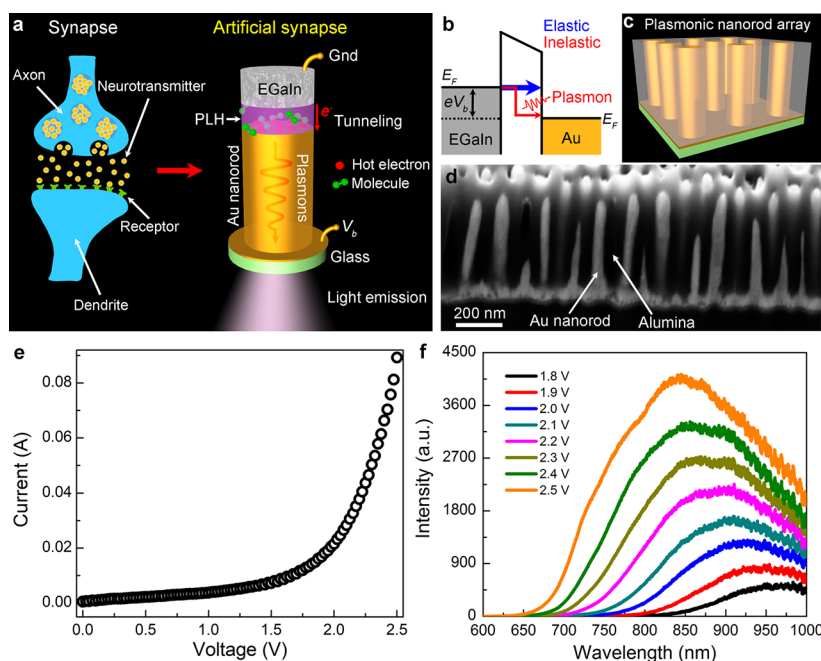
tronic or photonic systems. Recently, all-optical neuromorphic architectures based on synapses made of phase-changing materials was also demonstrated.<sup>8</sup> At the same time, the underlying feature of a biological synapse, particularly the changes of the resistivity depending on its chemical environment under the bias of the same polarity has remained elusive until now.

Here, we demonstrate a general principle of operation of a new type of memristive devices acting as artificial synapses for nonspiking ANNs by taking advantage of the chemical transformations induced by hot electrons in a tunnel junction. Using metal–polymer–metal tunnel junctions, we show the simultaneous multistate switching of the resistance and built-in light emission of the junctions, which is realized both electronically and optically by programming the junctions via hot-electron-mediated chemical reactions controlled by the environment. As hot electrons can be generated either electrically or optically and the tunnel junction has distinct electric response as well as acts as a nanoscale light source, the proposed approach allows several independent and interchangeable operation modalities in the same device with an electronic (optical) programming and electronic (optical) readout, as well as electronic (optical) programming and an

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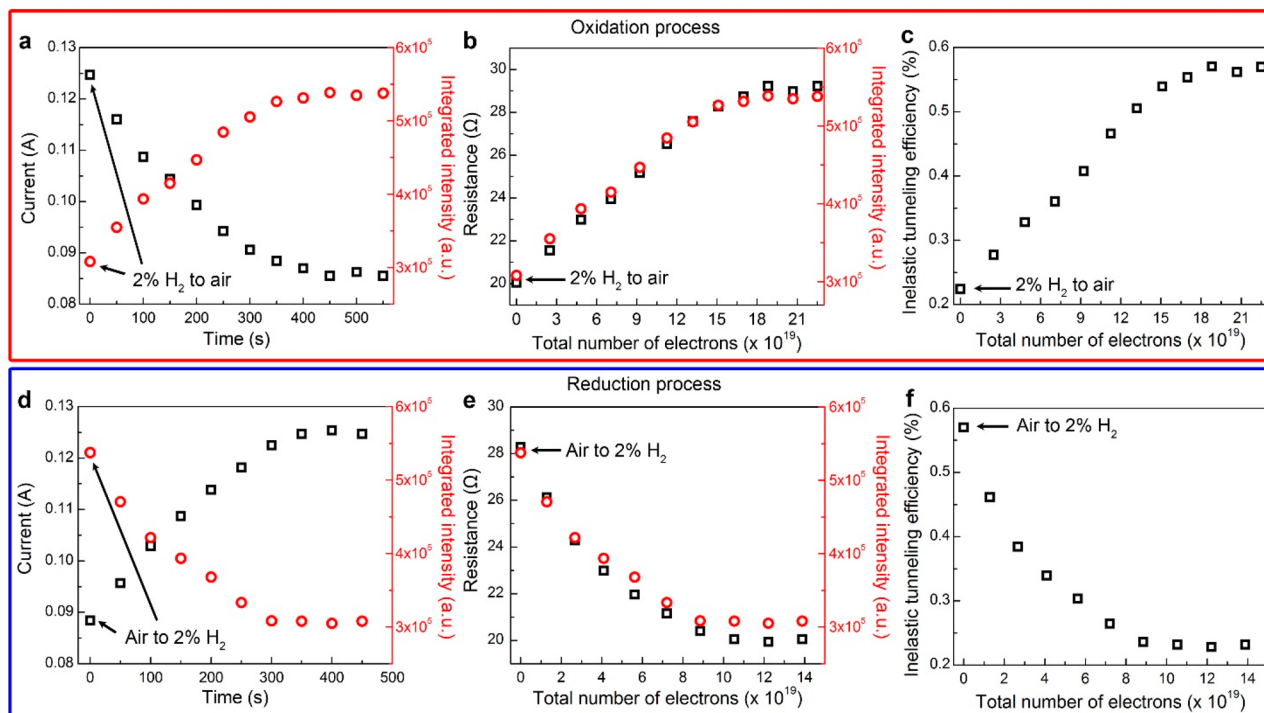
**Figure 1.** Memristor structure and light emission properties. (a) Schematic diagram of the memristive light-emitting tunnel junction, which is an optoelectronic analogue to a biological synapse (EGaIn and PLH denote eutectic gallium indium and poly-L-histidine, respectively). (b) Energy level diagram of the tunnel junction under a bias of  $V_b$ . (c) Schematic diagram of the plasmonic nanorod array used to realize multiple tunnel junctions. (d) Cross-sectional SEM view of a nanorod array. (e) Measured current–voltage characteristic of a tunneling device fabricated using the array shown in (d). (f) Measured emission spectra of the tunneling device as a function of the applied forward bias.

optical (electronic) readout. Changing chemical (in this case gas) environment, an increased or decreased response or a nonvolatile state can be achieved under the bias of the same polarity.

A biological synapse is the functionalized junction between an axon of a presynaptic neuron and a dendrite of a postsynaptic neuron (Figure 1a, left), which deals with the communications between neurons via neurotransmitters and acts as both a computing and memory unit. Light-emitting tunnel junction (Figure 1a, right), an optoelectronic analogue of a biological synapse, was constructed based on a plasmonic nanorod. During the tunneling process (Figure 1b), the inelastically tunneled electrons excite plasmons in the nanorod, which can subsequently decay radiatively into photons, whereas those electrons that tunnel elastically generate hot electrons in the tips of the nanorods. The hot electrons can be harvested for inducing chemical reactions in a chosen gas environment, which will influence the resistivity of the tunnel junction to a predefined level. In this way, the multilevel writing of the junction state can be achieved by changing the gas environment to promote oxidation or reduction reactions or to keep the nonreactive state under or without an applied bias. In the latter case, the stored information state is nonvolatile and can be read both electrically and optically by interrogating the resistance and emission intensity. In this sense, the light-emitting tunnel junction is an analogue of a biological synapse where the resistance between the axon and the dendrite is adjustively controlled by the release of the chemical species and the strength of the transmitted signal. Similarly, in the proposed artificial synapse, the tunneling resistance of the junction is controlled by the introduction of gas in conjunction with the strength of the passing tunneling current. Optical coding of the tunnel junctions is also possible using hot

electrons generated in the tunnel junctions by an external illumination in the respective gas environments.

Experimentally, tunnel junctions were constructed in a plasmonic nanorod array (Figure 1c), which was fabricated by electrodeposition of Au into porous alumina templates (see Supporting Information section 1). Figure 1d presents a cross-sectional view of a plasmonic nanorod array, clearly showing the Au nanorods embedded in the alumina template. The diameter, length, and separation of the nanorods are approximately 65, 480, and 105 nm, respectively. Metal–polymer–metal tunnel junctions were constructed on the surface of this nanorod metamaterial by using a monolayer of poly-L-histidine (PLH) as the tunnel barrier and “storage” layer (used as a reactant to store information via reconfigurable chemical reactions) and a droplet of eutectic gallium indium (EGaIn) as the top electrode (see Supporting Information section 2 for details). Each Au nanorod forms a tunnel junction with the top EGaIn contact (Figure 1a), creating an array of tunnel junctions (Supporting Information section 3) with density determined by the density of the Au nanorods in the metamaterial on the order of  $\sim 10^{10} \text{ cm}^{-2}$  (estimated from the SEM images as shown in Figure S1). A nonlinear current–voltage characteristic (Figure 1e) confirms the tunneling of electrons through the metal–polymer–metal junctions.<sup>24</sup> Upon the application of a forward bias, light emission was observed from the substrate side of the device, which is due to the radiative decay of plasmons excited in the nanorod metamaterial<sup>25–30</sup> (Figure 1b). The recorded emission spectra (having a line width of  $\sim 200 \text{ nm}$ ) as a function of the applied bias are shown in Figure 1f. With the increase of the bias, the emission intensity increases gradually, accompanied by a blue shift of the emission peaks following the quantum cutoff law,  $h\nu_{\text{photon}} \leq eV_b$ .<sup>25</sup> The spectrum of the emission is determined by the product of the emission power spectrum of the



**Figure 2.** Hot-electron-mediated programming of electrical and optical properties. (a) Time-dependent evolution of the tunneling current and integrated emission intensity during the hot-electron-mediated reaction of the tunnel junctions with oxygen (environment switched from 2%  $\text{H}_2$  gas to air). (b,c) Dependence of the resistance and integrated emission intensity (b) and the inelastic tunneling efficiency (c) on the total number of the tunneled electrons. (d) Time-dependent evolution of the tunneling current and integrated emission intensity during the hot-electron-mediated reaction of oxidized tunnel junctions with hydrogen (environment switched from air to 2%  $\text{H}_2$ ). (e,f) Dependence of the resistance and integrated emission intensity (e) and the inelastic tunneling efficiency (f) on the total number of the tunneled electrons.  $V_b$  is fixed at 2.5 V in all measurements.

fluctuating tunneling current, the modal profile of the metamaterial, and the radiation efficiency of the excited modes.<sup>31</sup> The electron-to-photon conversion efficiency is estimated to be around  $10^{-6}$ , which is determined by the radiation efficiency ( $\sim 3.5 \times 10^{-4}$ , Supporting Information section 4) of the metamaterial, and can be improved by engineering the local density of optical states and radiation efficiency of the tunnel junctions.<sup>31</sup>

During the tunneling process, the majority of electrons ( $\sim 99\%$ ) tunnel elastically (Figure 1b),<sup>24–29</sup> appearing as hot electrons<sup>32,33</sup> in the tips of the Au nanorods, which can be used for programming the state of the tunnel junctions via hot-electron-activated chemical reactions.<sup>34,35</sup> To use the hot-electron effects, the tunneling device was put into a gas chamber under a bias of 2.5 V, with the tunneling current and emission spectrum monitored simultaneously. The device was first stabilized in 2%  $\text{H}_2$  in  $\text{N}_2$ , and upon switching of a chamber environment to air, the tunneling current decreased gradually down to 2/3 of the original value (Figure 2a). At the same time, the integrated light emission intensity increased gradually to twice the original value. The changes in the tunneling current and emission intensity reflect a change in the junction state, which is due to the oxidation of the tunnel junctions by oxygen molecules in air mediated by hot electrons as a PLH monolayer undergoes oxidative dehydrogenation and coupling reactions.<sup>30</sup>

The resistance and emission intensity of the tunneling device depend on the total number of the tunneled electrons (Figure 2b) as the state of the tunnel junctions is dependent on the history of the tunneling process, particularly on how many

electrons have traversed the junctions before, demonstrating a memory effect similar to that in biological synapses. During the reaction, the device was brought from a low resistance state ( $\sim 20 \Omega$ ) to a high resistance state ( $\sim 29 \Omega$ ), with a simultaneous change in the light emission from a low intensity state to a high intensity state ( $\sim 80\%$  increase in the intensity). In this case, the written state of the tunnel junctions can be read out both electrically and optically, which is attractive for use as memory devices or artificial synapses, not only in electronic but also in optoelectronic systems. Moreover, compared with the existing optical memristors, which require external light sources for the optical readout,<sup>19–22,36</sup> the plasmonic tunnel junctions have nanoscale built-in plasmonic light sources, providing advantage for the dramatic reduction in the device size and power consumption (the operation power for single tunnel junction is around 600 pW; see Supporting Information section 4 for details). Normally, the emission intensity changes linearly with the tunneling current; however, the emission intensity shows an opposite trend to that of the current during the reaction. This can be understood considering the evolution of the estimated inelastic tunneling efficiency during the programming process (Figure 2c; see Supporting Information section 5 for details). During the reaction of the tunnel junctions with oxygen molecules, the inelastic tunneling efficiency increases gradually, resulting in the increased light emission intensity despite the gradual decrease of the tunneling current.

The tunneling device can be programmed back to the original state via the hot-electron-mediated reduction of the oxidized tunnel junctions when hydrogen molecules are



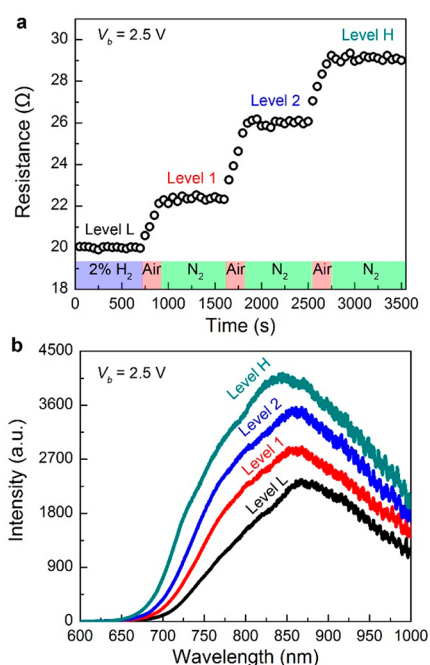
introduced into the gas cell (Figure 2d–f). The resistance, integrated emission intensity, and inelastic tunneling efficiency (Figure 2e,f) decreased gradually back to the original value with the continuous supply of the hot electrons and hydrogen molecules, highlighting the ability to reversibly program the tunneling device. The dynamics of the light-emitting reactive tunnel junctions can be associated with long-term potentiation/depression processes of synapses in a biological neural network. Different from ferroelectric or magnetic tunnel junctions based memristors exploiting tunnel electroresistance or magnetoresistance effects,<sup>12,13</sup> the light-emitting plasmonic tunnel junctions exploit elastically tunneled electrons for the writing of information and inelastically tunneled electrons for the optical readout, providing programmability of the response and sensitivity to the environment. It is worth noting that the relatively long time taken for the writing of information (Figure 2a,d) is due to the slow diffusion of gas molecules into the large-area highly confined tunnel junction array, which should be improved by reducing the surface area of the device or patterning the device into a crossbar structure for the quicker diffusion of gases into the junctions.

As discussed above, the state of the tunnel junctions is highly dependent on the number of the tunneled electrons and the environment. By controlling the supply of hot electrons or reactants (oxygen or hydrogen), the tunneling device can be latched to different intermediate states. For example, as shown in Figure 3a, the resistance of the device was switched from  $\sim 20\ \Omega$  (low resistance state, level L) to 22 (level 1), 26 (level 2), and 29  $\Omega$  (high resistance state, level H) by controllably introducing oxygen molecules into the chamber for the oxidation of the tunnel junctions. When the required state

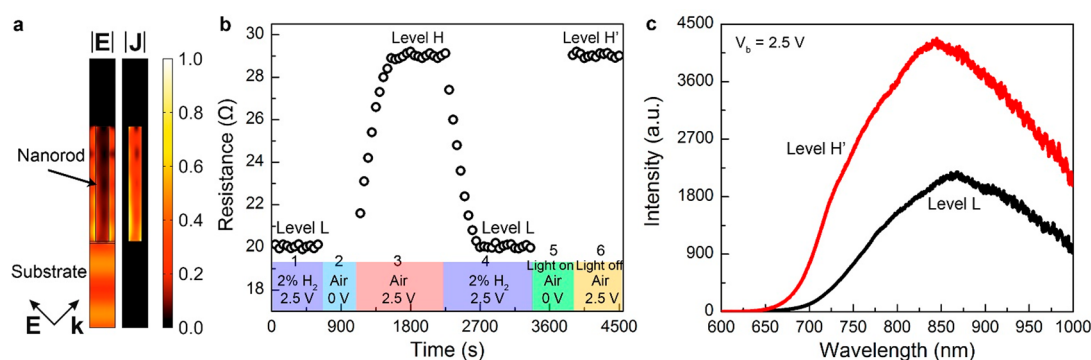
was achieved, pure nitrogen (employed as a nonreactive environment) was introduced into the chamber to remove oxygen molecules in order to latch the state of the junctions. Under the nonreactive environment of nitrogen, the state of the junctions was maintained when the bias was switched off (see Supporting Information section 6), showing the non-volatility. Accordingly, the light emission from the device was also latched to different intermediate levels (Figure 3b). The slight shift in the emission peak is due to the modification of the local density of optical states in the junctions by the chemical reactions. Taking advantage of the programming mechanism of the reactive tunnel junctions, the states of the junctions may, in principle, be controlled on a single electron or molecule level. Therefore, the number of levels can be regulated by either the tunneling current (therefore, a bias), the interaction time, and even the quantity of the reactive gases introduced into the junctions, with the maximum number ultimately determined by the noise in the readout signal. Instead of carrying out computations based on binary logic in digital chips, the artificial synapses based on reactive tunnel junctions work in a way analogous to neurons in the brain that activate in various ways depending on the type and number of ions that flow across a synapse.

Apart from the electrochemical programming, the state of the tunnel junctions can be programmed optically. Under external light illumination of the nanorod metamaterial from the substrate side, the plasmonic modes in the metamaterial are excited. Figure 4a shows the simulated electric field and current distributions in the unit cell of the metamaterial illuminated by light with a wavelength of 600 nm at which the extinction has a maximum (see Supporting Information section 7 for details). The plasmonic excitation exists across the whole nanorod length, and hot electrons are generated not only at the side walls in the lower part of the nanorods but also at their tips; the latter can be used directly for the activation of chemical reactions in the tunnel junctions.<sup>37</sup> In order to demonstrate this (Figure 4b), the device was first stabilized in 2%  $\text{H}_2$  in  $\text{N}_2$  under 2.5 V (period 1). The state of the junctions was unchanged when the environment was switched to air under a zero bias (period 2) due to the lack of hot electrons for the reaction. Under the applied bias, the gradual rise of the tunnel resistance to level H was observed as expected (period 3). The junction state was programmed back to the low resistance level (period 4) by introducing 2%  $\text{H}_2$  back into the chamber under the applied bias. However, when the environment was switched to air under a zero bias but the metamaterial was illuminated by a broadband light (500–750 nm, matched with the extinction peak) with a power density of  $\sim 0.02\ \text{W}/\text{cm}^2$  (period 5), the state of the junctions was programmed to the high resistance level (confirmed by the stable resistance after the removal of illumination under a bias of 2.5 V (period 6)). The spectra of the latched light emission corresponding to the level L and optically switched level H' agree well with the emission spectra from the electrically programmed low and high resistance levels (cf. Figure 4c and Figure 3b). The ability of optical coding provides an alternative choice for the writing of information with advantages such as wireless and wavelength-dependent control.

In conclusion, we have investigated the electrical and optical memory effects in reactive plasmonic tunnel junctions. The high density of tunnel junctions ( $\sim 10^{10}\ \text{cm}^{-2}$ ) and scalability provided by the plasmonic nanorod array make the proposed approach a promising platform for the construction of



**Figure 3.** Multilevel programming of the electrical and optical properties. (a) Continuous switching of the resistance of the tunneling device by controlling the environment. The device was first stabilized in 2%  $\text{H}_2$  ( $V_b = 2.5\ \text{V}$ ), and the resistance was switched by the introduction of oxygen molecules and latched by replacing oxygen environment with nitrogen. (b) Corresponding latched emission spectra of the tunneling device.



**Figure 4.** Optical programming of the tunneling device. (a) Normalized simulated electric field  $|E|$  and current  $|J|$  distributions in the unit cell of the metamaterial illuminated by light with a wavelength of  $\lambda = 600$  nm. (b) Evolution of the resistance of the tunneling device under different conditions, as indicated at the bottom. White light illumination in the spectral range of 500–750 nm and power density of  $\sim 0.03$  W cm $^{-2}$  was used during period 5. (c) Emission spectra of the tunneling device measured at the resistance level L and the optically programmed resistance level H'.

neuromorphic computing devices. A direct analogy can be considered between multiple tunnel junctions connected to the same back electrode and multiple biological synapses connected to a neuron. Additionally, by patterning the nanorod array<sup>38</sup> and the top electrodes into micro- or nanoscale crossbars,<sup>6,7</sup> it is possible to configure the plasmonic nanorod array into a network of tunnel junction units formed at each crosspoint which can be addressed individually with both electrical and optical approaches (despite the global gas environment, the information is written only when individual units are addressed). The proposed programmable tunnel junctions may be applied as both memristive multilevel devices in traditional electronic circuits as well as artificial synapses for nonspiking ANNs. The light-emitting reactive tunnel junctions can also be integrated directly with plasmonic or silicon waveguides to deliver or collect optical signals for the application as memory, logic units, and artificial synapses in optoelectronic systems, scaled down to single junctions if required.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.nanolett.9b03871>.

Fabrication of plasmonic nanorod metamaterials; fabrication of metal–polymer–metal tunnel junctions; nanorod–metamaterial-based tunneling device; estimation of inelastic tunneling efficiency; nonvolatility of the device; numerical simulations (PDF)

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### Notes

The authors declare no competing financial interest.

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