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# Reactive tunnel junctions in electrically-driven plasmonic nanorod metamaterials

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**Hot, nonequilibrium carriers formed near the interfaces of semiconductors or metals play a crucial role in chemical catalysis and optoelectronic processes. In addition to optical illumination, an efficient way to generate hot carriers is by excitation with tunnelling electrons. Here we show that the generation of hot electrons makes the nanoscale tunnel junctions highly reactive and facilitates strongly confined chemical reactions which can in turn modulate the tunnelling processes. We designed a device containing an array of electrically-driven plasmonic nanorods with up to  $10^{11}$  tunnelling junctions per square centimeter, which demonstrates hot-electron activation of oxidation and reduction reactions in the junctions, induced by the presence of  $O_2$  and  $H_2$  molecules, respectively. The kinetics of the reactions can be monitored in-situ following the radiative decay of tunnelling-induced surface plasmons. This electrically-driven plasmonic nanorod metamaterial platform can be useful for the development of nanoscale chemical and optoelectronic devices based on electron tunnelling.**

23 Quantum-mechanical tunnelling enables the transport of electrons across a nanoscale gap between two  
24 conducting electrodes. The broadband fluctuations in the tunnelling current can excite surface plasmons  
25 —the collective oscillations of free electron gas—in metallic nanostructures, providing a method for  
26 plasmon excitation with several distinct advantages, including high compactness, fast response, and free  
27 of background noise<sup>1-5</sup>. The electron-to-plasmon conversion efficiency is only about one plasmon per  
28  $10^5$  electrons in metal-dielectric-metal junctions<sup>1,5</sup> and scanning-tunnelling-microscope experiments<sup>2-4</sup>.  
29 However, this can be improved by one or two orders of magnitude by nanostructure design (using single  
30 optical antennas or their microscale arrays)<sup>6-8</sup>. In addition, assembling such electrically-driven  
31 nanoantennas using metamaterial approaches on a macroscopic scale would allow additional flexibility  
32 in engineering the local density of optical states, a crucial step to efficient surface plasmon generation.

33 Optically excited surface plasmons have recently been proposed for the efficient generation of hot  
34 carriers<sup>9-11</sup>, which can be productively used for chemical catalysis and optoelectronics<sup>9,10,12-17</sup> if  
35 extracted from the metal into its surroundings before they thermalize by heat generation<sup>10,18</sup>. During the  
36 tunnelling process, the majority of electrons tunnel elastically (maintaining their energy), appearing as  
37 energetic hot electrons in the receiving electrode<sup>19</sup>. Therefore, tunnel junctions can be used to harvest  
38 hot electrons for the controllable activation of highly-confined chemical reactions. Since tunnelling is  
39 extremely sensitive to any changes in the nanometer scale tunnelling gap<sup>20,21</sup>, it can be significantly  
40 influenced by chemical processes, thus affecting surface plasmon generation due to inelastic tunneling  
41 and related light emission. In this manner, tunneling can be used for real-time detection of  
42 environmental changes at the molecular level in the junctions, serving as both nanoreactors and sensors,  
43 and for the investigation of hot-electron effects.

44 One prospective metamaterial design to maximally exploit tunnelling effects is an array of

45 electromagnetically coupled nanorods in which each nanorod functions both as a tunnel tip and as an  
46 optical antenna (Fig. 1a,b). The typical nanorod areal densities are as high as  $10^{10}$  to  $10^{11}$   $\text{cm}^{-2}$ , while the  
47 metamaterials can cover macroscopic areas due to the scalable electrochemical fabrication technique.  
48 The large surface area provided by this type of metamaterial and the responsiveness to refractive index  
49 changes have already been employed for record-sensitivity biological<sup>22</sup> and chemical<sup>23</sup> sensing,  
50 ultrasound detection<sup>24</sup> as well as for water splitting<sup>12</sup>.

51 Here, by taking advantage of high-density Au nanorod arrays, we demonstrate the stimulation of  
52 hot electrons, surface plasmons and light emission in the metamaterials by electron tunnelling over a  
53 macroscopic (up to  $\sim 1$   $\text{cm}^2$ ) surface area. The large flux of hot electrons makes the tunnel junctions  
54 highly reactive as demonstrated here on the example of strongly confined oxidation and reduction  
55 reactions involving  $\text{O}_2$  and  $\text{H}_2$ , respectively. These reactions are monitored either optically by changes in  
56 the intensity of light emission ( $\sim 50\%$ ) resulting from the radiative decay of tunnelling-generated surface  
57 plasmons, or electrically via tunnelling current variations ( $\sim 10\%$ ).

58

### 59 **Design of electrically-driven nanorod metamaterials**

60 Experimentally, the plasmonic nanorod metamaterials were fabricated by direct electrodeposition of Au  
61 into substrate-supported porous  $\text{Al}_2\text{O}_3$  templates (see Methods and Supplementary Section 1). Figure 1c  
62 shows the surface morphology of an ion-milled (Supplementary Section 2) metamaterial (nanorod  
63 diameter  $d \approx 50$  nm, length  $l \approx 420$  nm, and separation between the nanorods  $s \approx 100$  nm). The nanorod  
64 tips are several nanometers lower than the surrounding  $\text{Al}_2\text{O}_3$  matrix (Supplementary Fig. 1). The  
65 optical transmission spectra obtained with TM polarized light (Fig. 1d) are dominated by two  
66 nearly-merged polarization-dependent extinction peaks as the metamaterial is strongly anisotropic<sup>25,26</sup>.

67 The reflection spectra reveal the two guided modes supported by the metamaterial slab when  
68 illuminated in the attenuated total internal reflection geometry. The counterparts of these modes also  
69 exist within the light cone in the low wave-vector region, corresponding to relatively low quality-factor  
70 Fabry-Perot modes<sup>26</sup>.

71 Taking advantage of the nanometer-scale height difference between the Au nanorods and the  
72 surrounding Al<sub>2</sub>O<sub>3</sub> matrix (Fig. 1c), it is straightforward to construct electrically-driven plasmonic  
73 nanorod metamaterials based on metal-air-metal tunnel junctions by using liquid eutectic  
74 gallium-indium (EGaIn) as a top contact<sup>5</sup> (Fig. 2a, see Methods and Supplementary Section 3). When a  
75 bias is applied between the Au nanorods and EGaIn, electrons tunnel across the nanometer-scale air  
76 gaps from occupied states in EGaIn to unoccupied states in Au nanorods (Fig. 2b). The majority of  
77 electrons tunnel elastically, appearing as hot electrons in the Au nanorods. The electrons which tunnel  
78 inelastically can excite plasmonic modes in the nanorods forming the metamaterial. The excited  
79 plasmons can then either radiate into free-space light via the metamaterial slab modes or decay into hot  
80 carriers in the nanorods.

81

## 82 **Electric excitation of plasmons in metamaterials**

83 A typical current–voltage curve for the device (Fig. 2c) shows that the measured current increases  
84 nonlinearly with the increasing bias, confirming electron tunnelling through the air gaps<sup>27</sup>. The  
85 experimental result is in excellent agreement with numerical simulations of the electron tunnelling  
86 process (Fig. 2c, see Supplementary Section 4), in which the averaged thickness of the air gaps was  
87 estimated to be around 1.15 nm. Strong light emission of a distinctly red colour (an area of  
88 approximately 4 mm<sup>2</sup>) was observed from the substrate side when a bias of 2.5 V was applied (inset of

89 Fig. 2c). The observed emission is due to the excitation of a metamaterial plasmonic mode via the  
90 inelastic tunneling process, which subsequently radiates into free space (Fig. 2b). Due to the large  
91 number of effective nanoscale tunnel junctions in the metamaterial (nanorod areal density  
92 approximately  $1.3 \times 10^{10} \text{ cm}^{-2}$ ), the emission is visible to the naked eye, making signal detection trivial  
93 for practical applications as well as providing a large surface area comprised of multiple nanorods for  
94 the extraction of hot electrons. The efficiency of the inelastic tunnelling process is estimated to be about  
95 0.1% (Supplementary Section 5), a value which qualitatively agrees with previous experimental  
96 observations<sup>7</sup> and theoretical predictions<sup>28,29</sup>.

97 The emission spectra measured under varying forward bias (Fig. 2d and Supplementary Section 6)  
98 are relatively broad, typical for tunnelling-based excitation. With an increasing applied bias, the  
99 intensity of emission increases gradually (Supplementary Fig. 4), and is accompanied by a blue-shift of  
100 the cutoff wavelength. This is expected for light emission generated by inelastic tunnelling electrons<sup>1,5-7</sup>,  
101 as the energies of the emitted photons are always less than the energy of tunnelling electrons (see  
102 Methods and Supplementary Section 8). The simulated spectra of the tunnelling-electron-induced  
103 emission are in excellent agreement with the experimental observations (Fig. 2e); their shape is defined  
104 by the product of the emission spectrum of the tunnelling current source, the modal profile of the  
105 metamaterial and the radiation efficiency of the excited modes<sup>7</sup> (see Methods). Particularly, the field  
106 map of the  $E_x$  component of the electric field (Fig. 2f) related to the cylindrical plasmon modes of the  
107 nanorods, clearly shows that the maximum emitted intensity (Fig. 2e) corresponds to the coupling of the  
108 tunnelling-excited surface plasmons to the metamaterial mode (mode 3), which facilitates radiation into  
109 the far-field measured in the experiment.

110

## 111 **Hot-electron-activated reactive tunnel junctions**

112 Considering that the inelastic tunnelling efficiency is estimated to be  $\sim 0.1\%$ , approximately 99.9% of  
113 the electrons tunnel elastically appearing as hot electrons in the nanorod tips. Under a forward bias of  
114 2.5 V (tunnelling current of  $\sim 0.085$  A, Fig. 2c), hot electrons are generated at a rate of  $\sim 10^9$  s<sup>-1</sup> in the tip  
115 of each nanorod with the same energy of 2.5 eV (different from the plasmon-induced hot electrons with  
116 broad energy and spatial distributions<sup>30</sup>). The highly efficient and confined hot-electron generation  
117 makes the tunnel junctions highly reactive and opens up opportunities for modulating the tunnelling  
118 processes via the hot-electron-activated reactions. To demonstrate this capability, we stimulated  
119 hot-electron-driven oxidation and reduction reactions involving O<sub>2</sub> and H<sub>2</sub> in the junctions which were  
120 monitored in real time by observing the modified light emission from the metamaterial.

121 To make use of the hot electrons for chemical reactions, metal-polymer-metal tunnel junctions  
122 were constructed (Fig. 3a) allowing to access the tunnelling region instead of the closed metal-air-metal  
123 tunnel junctions (Fig. 2a). Beginning with a nanorod metamaterial ( $d \approx 66$  nm,  $l \approx 480$  nm,  $s \approx 105$  nm),  
124 the Al<sub>2</sub>O<sub>3</sub> matrix was first chemically etched in order to expose the Au nanorod tips (Supplementary  
125 Section 10), so that they were  $\sim 10$  nm higher than the surrounding template facilitating the interaction of  
126 tunnel junctions with the gas molecules (Fig. 3b). The nanorod tips were then functionalized with a  
127 monolayer of poly-L-histidine (PLH) which works both as a tunnel barrier and a reactant (see Methods  
128 and Supplementary Section 11), and finally a droplet of EGaIn was added on top. Under an applied bias,  
129 a nonlinear current–voltage curve and associated light emission were observed from the device  
130 (Supplementary Fig. 8), confirming tunnelling process in the functionalized nanorod tips.

131 The electrically-driven metamaterial was then placed in a gas cell and both the tunnelling current  
132 and the light emission spectrum were monitored simultaneously (Supplementary Section 13). At the

133 beginning, the cell was purged with 2% H<sub>2</sub> in N<sub>2</sub> atmosphere and then maintained in pure N<sub>2</sub>. When O<sub>2</sub>  
134 was subsequently introduced into the gas cell with air, the emission intensity gradually increased  
135 reaching twice the original value (Fig. 3c). Then, following the reintroduction of 2% H<sub>2</sub> in N<sub>2</sub>, the light  
136 emission intensity decreased back to the initial value (Fig. 3d). By cycling the cell atmosphere between  
137 air with 26% relative humidity (RH), N<sub>2</sub>, 2% H<sub>2</sub> in N<sub>2</sub>, O<sub>2</sub>, and 2% H<sub>2</sub> in N<sub>2</sub> with 75% RH (Fig. 3e), it  
138 was confirmed that the observed changes of the emission intensity, which reflect the modification of the  
139 tunnel junctions, were caused by the reaction of tunnel junctions with O<sub>2</sub> and H<sub>2</sub> molecules  
140 (Supplementary Section 14). It is worth noting that it takes several minutes to complete the reactions  
141 due to the highly-confined metal-PLH-metal tunnel junctions which hinders the fast diffusion of gas  
142 molecules.

143 We have also investigated the effect of the applied bias on the induced chemical processes. This  
144 was conducted by firstly measuring the stabilized emission spectrum characteristic of the tunnel  
145 junctions in an environment of ambient air or 2% H<sub>2</sub> in N<sub>2</sub> at an applied sensing bias of 2.5 V. Then, the  
146 bias was varied to a predetermined test value (2.5, 2.0, 1.5, 1.0, 0.5, and 0 V), the cell atmosphere was  
147 exchanged, and the device was kept under this bias for 10 minutes. In order to interrogate the tunnel  
148 junction state after the test period, the bias was changed back to 2.5 V, and a sequence of emissions  
149 spectra were recorded every 50 s until the device reached saturation. Figure 4a shows the percentage  
150 change in emission intensity during the 10-min period under different value of test bias (plotted from  
151 Supplementary Fig. 10). It was observed that the chemical reactions involving O<sub>2</sub> (blue bars in Fig. 4a)  
152 and H<sub>2</sub> (red bars in Fig. 4a) molecules are highly dependent on the applied bias; the higher the bias, the  
153 faster the rate of the reaction. The bias-dependent response is highly indicative of the role of the  
154 hot-electron energy on the reactions which depends on the voltage applied to the tunnel junction, as was

155 discussed above.

156 In order to further verify the role of hot electrons in the reactions, we studied the reactions in the  
157 unbiased ( $V_b = 0$  V, no tunnelling-induced hot electrons) tunnel junctions while under external  
158 illumination which can generate hot electrons via the optically excited plasmons (Supplementary  
159 Section 15). The response to the reaction with  $O_2$  is highly dependent on the illumination wavelength  
160 (blue bars in Fig. 4b and Supplementary Figs. 11a–d). The emission intensity increased 100% to the  
161 highest level during the test period when the surface plasmons related to the nanorods forming the  
162 metamaterial were efficiently excited (500-750 nm illumination, see inset of Fig. 4b), whereas in the  
163 case of less efficient plasmonic excitation (>800 nm illumination), the emission intensity change is  
164 almost the same as without illumination. This directly confirms the role of hot electrons in the chemical  
165 reaction involving the  $O_2$  molecules: when the device is operated under 2.5 V in  $N_2$ , hot electrons are  
166 mainly generated in the Au nanorod tips via the elastic tunnelling of electrons<sup>19</sup> (Fig. 2b and process 1 in  
167 Fig. 4c); upon the switching of cell atmosphere from  $N_2$  to air,  $O_2$  molecules diffuse into the tunnel  
168 junctions and interact with the hot electrons, forming transient negative  $O_2^-$  species facilitated via  
169 hot-electron transfer from the Au to the antibonding orbital of  $O_2$  and eventually dissociated into O  
170 atoms<sup>14,31,32</sup>. The O atoms subsequently form Au oxides with the surface atoms of Au nanorod tips  
171 (although Au is the most resistant noble metal to oxidation in air even at elevated temperature, Au  
172 oxides can be formed in highly reactive environments<sup>33,34</sup>), while the Au oxides can in turn oxidize the  
173 PLH monolayer (NH group in the imidazole rings and/or amino groups of PLH near the nanorod tips  
174 can undergo oxidative dehydrogenation and coupling reactions)<sup>14,31,34–36</sup>. The oxidation of the tunnel  
175 junctions finally causes a change in the tunnelling barrier that subsequently changes the plasmon  
176 excitation and, therefore, the light emission intensity (process 2 in Fig. 4c, optically revealed in Fig. 3c).

177 The reaction induced by H<sub>2</sub> molecules is not influenced by the external illumination (red bars in Fig. 4b  
178 and Supplementary Figs. 11e–h). This is due to the formation of Au oxides after reaction in air which  
179 can hinder the interaction of plasmon-induced hot electrons with H<sub>2</sub> molecules. And the  
180 plasmon-assisted heat generation under the external illumination condition ( $\sim 0.1 \text{ W cm}^{-2}$ ) is not enough  
181 to activate the reaction of H<sub>2</sub> molecules with the Au oxides. However, in the case of tunnelling (electric  
182 power density of  $\sim 5.6 \text{ W cm}^{-2}$  under an applied bias of 2.5 V), the elevated temperature in the tunnel  
183 junctions ( $\sim 63^\circ\text{C}$ , see Supplementary Section 16), mainly due to the relaxation of the hot electrons<sup>37</sup>, can  
184 improve the reactivity of H<sub>2</sub> molecules facilitating the reduction of Au oxides (because of the Arrhenius  
185 dependence of rate constants on temperature<sup>38,39</sup>). This subsequently makes the hot electrons accessible,  
186 resulting in the dissociation of H<sub>2</sub> molecules into H atoms<sup>13,40</sup> and then the full recovery of the tunnel  
187 junctions (hydrogenation of the oxidized PLH monolayer back to PLH) together with the plasmon  
188 excitation and light emission (process 3 in Fig. 4c, optically revealed in Fig. 3d). At the same time,  
189 metastable gold hydride can form due to the absorption of H atoms on the nanorod tips<sup>31,41</sup> (process 4 in  
190 Fig. 4c), evidenced by the emission intensity change when the device was purged with N<sub>2</sub> after the  
191 reaction with H<sub>2</sub> molecules (black circles in Fig. 3e). It can be estimated that about  $10^{-5}\%$  of the input  
192 electric energy is used for the chemical reactions during the reaction period limited by small number of  
193 available molecules in the nanojunctions (Supplementary Section 17). The chemical reactions influence  
194 both the light emission intensity and the tunnelling current when the cell atmosphere was cycled  
195 between air and 2% H<sub>2</sub> (Fig. 4d). The change of the emission intensity exhibits an opposite trend to that  
196 of the current, which may be attributed to the difference in the inelastic tunnelling efficiencies through  
197 pristine and oxidized tunnel junctions.

198 The nanoscale reactive tunnel junctions demonstrated above can also be considered for gas sensing.

199 Due to the high spatial confinement of the electron tunnelling process and its extreme sensitivity to the  
200 junction properties<sup>20,21,42</sup>, as well as the abundant energetic hot electrons in the junctions, it is promising  
201 to develop sensors based on electrically-driven plasmonic nanorod metamaterials with atomic level  
202 sensitivity and small footprint. As shown in Fig. 4d, the changes in the emission intensity are about 5  
203 times higher than that of the tunneling current (50% vs 10%), indicating the high sensitivity of optical  
204 detection for tunnelling-based sensors (the non-optimized sensitivity for H<sub>2</sub> sensing demonstrated here  
205 is about two times higher than the previous result based on Pd-coated Au nanorod metamaterials<sup>23</sup>). In  
206 addition, by choosing an appropriate material for the functionalization of tunnel junctions, the device  
207 can be designed to transduce a variety of chemical and physical stimuli (e.g., gas, molecule, light, or  
208 pressure).

209

## 210 **Conclusions**

211 We have demonstrated the potential for controlling chemical reactions at the nanoscale using  
212 tunnelling-driven generation of hot electrons in metal-polymer-metal gaps. By monitoring either the  
213 changes in the tunnelling current or the light intensity due to radiation of the excited plasmonic modes,  
214 we have demonstrated both optical and electrical detection schemes that allow for a precise monitoring  
215 of the tunnel junction's reactive properties. In addition to the sensing applications, it is evident that the  
216 electrically-driven metamaterial platform can also be used as an array of nanoreactors. It can be applied  
217 for the *in-situ* studies and real-time monitoring of chemical transformation of molecules functionalized  
218 in the junctions, such as the oxidation of aromatic amines or the reduction of aromatic nitro compounds  
219 to produce aromatic azo dyes<sup>31</sup>; it can also be applied for the activation of gas phase reactions such as  
220 the degradation of volatile organic compounds (e.g., HCHO and CO)<sup>14</sup>. Thus, it can work as a

221 lab-on-a-chip device to assist in developing and understanding new chemical reactions where precise  
222 stimulation and monitoring is paramount. In addition to operation in a gas environment or vacuum, it is  
223 also possible to use the electrically-driven metamaterial platform for the activation of reactions in liquid  
224 environments (such as ethanol, see Supplementary Section 18). By reciprocity, the metamaterial is also  
225 capable of harvesting far-field radiation into localized energy such as hot electrons and heat, which is of  
226 interest for applications such as photodetection and thermoelectricity<sup>17,43,44</sup>. Combining the high  
227 sensitivity of tunnel junctions with a compact electric excitation method and the large surface area for  
228 hot-electron extraction provided by nanorod metamaterials, the described metamaterial platform merges  
229 electronics, plasmonics, photonics, and chemistry for the study and manipulation electrons, plasmons,  
230 and photons at the nanoscale.

231

232

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332

### 333 **Author contributions**

334 A.V.Z. and P.W. conceived the study. P.W. constructed the experiment, performed the measurement and  
335 analyzed the data. M.E.N. and W. D. fabricated the plasmonic nanorod metamaterials. A.V.K. performed  
336 numerical simulations. All the authors discussed the results and co-wrote the paper.

337

### 338 **Additional information**

339 Supplementary information is available in the online version of the paper. Reprints and permission  
340 information is available online at [www.nature.com/reprints](http://www.nature.com/reprints). Correspondence and requests for materials  
341 should be addressed to P.W. or A.V.Z.

342

### 343 **Competing financial interests**

344 The authors declare no competing financial interests.

345

346 **Figure captions**

347

348 **Figure 1 | Structural and optical properties of plasmonic nanorod metamaterials.** **a**, Schematic  
349 diagram of the nanorod metamaterial, where  $d$  and  $l$  represent the diameter and length of the nanorods,  
350 respectively, and  $s$  is the separation between the nanorods. **b**, Cross-sectional view of a metamaterial  
351 showing Au nanorods embedded in a porous Al<sub>2</sub>O<sub>3</sub> template. **c**, Surface morphology of an ion-milled  
352 metamaterial analysed by atomic force microscopy. The dips are the tips of Au nanorods surrounded by  
353 Al<sub>2</sub>O<sub>3</sub>. **d**, Experimental dispersion of extinction (for the angles below total internal reflection) and  
354 reflection (for the angles above total internal reflection) of the metamaterial for TM-polarized  
355 illumination.

356

357 **Figure 2 | Electrically-driven nanorod metamaterial based on metal-air-metal tunnel junctions.**

358 **a,b**, Schematics of the device configuration (**a**) and the tunnelling processes (**b**). When a bias is applied  
359 between the EGaIn and Au nanorods, electrons tunnel across the junctions from occupied states in  
360 EGaIn to unoccupied states in Au nanorods. The majority of electrons tunnel elastically to form hot  
361 electrons in the Au nanorod tips; the inelastically tunnelling electrons excite surface plasmons in the  
362 metamaterial, which can then decay non-radiatively via the excitation of hot carriers or radiatively into  
363 photons from the substrate side of the metamaterial. **c**, Experimentally measured and theoretically  
364 calculated current–voltage curves for a device fabricated using the metamaterial shown in Fig. 1. Inset,  
365 photograph of the device with an applied bias of  $V_b = 2.5$  V. **d,e**, Measured (**d**) and simulated (**e**)  
366 emission spectra of the device as a function of the applied forward bias. **f**, Simulated near-field map of  
367 the metamaterial plasmonic mode excited via tunnelling and the subsequent radiation of the optical

368 signal into the far field.

369

370 **Figure 3 | Electrically-driven nanorod metamaterial with reactive tunnel junctions.** **a**, Schematic  
371 diagram of the device configuration based on metal-polymer-metal tunnel junctions. The  $\text{Al}_2\text{O}_3$  matrix  
372 was first chemically etched in order to expose the Au nanorod tips. The nanorod tips were then  
373 functionalized with a monolayer of poly-L-histidine (PLH) which works both as a tunnel barrier and a  
374 reactant. **b**, Surface morphology of an etched metamaterial with the exposed nanorod tips. **c,d**, The  
375 evolution of the emission spectra of the metamaterial ( $V_b = 2.5$  V) when the cell atmosphere was  
376 switched from  $\text{N}_2$  with 2%  $\text{H}_2$  to air (**c**) and from air to  $\text{N}_2$  with 2%  $\text{H}_2$  (**d**). **e**, Integrated emission power  
377 from the metamaterial measured when the cell atmosphere was dynamically changed between air,  $\text{N}_2$ , 2%  
378  $\text{H}_2$  in  $\text{N}_2$ ,  $\text{O}_2$ , and 2%  $\text{H}_2$  in  $\text{N}_2$  with 75% RH.

379

380 **Figure 4 | Electro-photo-chemistry in nanoscale tunnel junctions.** **a**, Changes of the emission  
381 intensity from the device during 10-min period for different test biases without external illumination,  
382 plotted from Supplementary Fig. 10. **b**, Changes of the emission intensity from the device during  
383 10-min period under various external illumination conditions without applied bias, plotted from  
384 Supplementary Fig. 11. Inset, experimental dispersion of extinction of the metamaterial for  
385 TM-polarized illumination. **c**, Schematics of the mechanism for the chemical reactions in the reactive  
386 tunnel junction. **d**, Tunnelling current (red hollow squares) and emission power (blue hollow circles)  
387 measured when the cell atmosphere was cycled between air and  $\text{N}_2$  with 2%  $\text{H}_2$  under  $V_b = 2.5$  V bias.

388

## 389 **Methods**

390 **Fabrication.** Plasmonic nanorod metamaterials were fabricated via Au electrodeposition into  
391 nanoporous Al<sub>2</sub>O<sub>3</sub> templates on a glass substrate<sup>22,24,25</sup>. Fabricated metamaterials were then ion-milled  
392 (V6000 mill & sputter system, Scientific Vacuum Systems) at an oblique angle of 75° with respect to the  
393 normal to the sample surface. Metal-air-metal tunnel junctions were fabricated by using EGaIn (≥ 99.99%  
394 trace metals basis, Sigma-Aldrich) as a top contact. Because the surface of EGaIn is protected by a  
395 native skin of highly conductive Ga<sub>2</sub>O<sub>3</sub> (<1 nm in thickness), it provides excellent structural stability to  
396 the liquid metal so that EGaIn can deform to match the metamaterial surface but not penetrate into the  
397 pores, making it possible to form nanometer-scale air gaps above the nanorod tips. Metal-PLH-metal  
398 tunnel junctions (Fig. 3a) were fabricated as follows: firstly, a wet chemical etching method was used to  
399 make the surrounding Al<sub>2</sub>O<sub>3</sub> matrix lower than the nanorod tips; secondly, the exposed Au nanorods  
400 were functionalized with a monolayer of PLH (M<sub>w</sub> = 5,000—25,000, Sigma-Aldrich) by self-assembly  
401 method to form a ~1.7-nm-thickness dielectric layer; finally, a droplet of EGaIn was added to form the  
402 top contact.

403 **Optical characterization.** The nanorod metamaterial was mounted vertically on a sample holder, which  
404 was then connected to a power supply for the electric excitation and an ammeter to monitor the  
405 tunnelling current. A 20X objective (NA = 0.28, Plan Apo SL, Nikon) was used to collect the light  
406 emission from the substrate side of the metamaterial, which was then redirected to a spectrometer (Triax  
407 332, Horiba Jobin Yvon) equipped with a charge-coupled device for spectral analysis. All the emission  
408 spectra were obtained using the same exposure time of 0.5 s, and then normalized using the spectral  
409 response function of the apparatus. The plots in Figs. 3e, 4d, S10 and S11 are the integrated intensity

410 over the measured emission spectra. The long-term and on-off switching stability of the device were  
411 also checked (Supplementary Fig. 6).

412 **Numerical simulations.** Upon inelastic tunnelling, the emission spectrum from the tunnel junction is  
413 defined by a product of the emission spectrum of the tunnelling current source (determined by the  
414 Fourier transform of the current fluctuations  $C(\omega) \sim \left(1 - \frac{\hbar\omega}{eV}\right)$ , where  $e$  is the electron charge,  $V$  is  
415 the applied bias, and  $\hbar$  is the Planck's constant<sup>28,45</sup>), the modal profile of the metamaterial (determined  
416 by the local density of states at the dipole position) and the radiative efficiency of the excited modes in  
417 free space<sup>7</sup>. Numerically, the emission spectrum was found by placing a dipole with a dipole moment  
418 determined by  $C(\omega)$  in the tunnelling area and integrating the optical power emitted within the angular  
419 range set by the numerical aperture used in the experiment<sup>6</sup>. The dipole characteristic position was  
420 chosen to be  $r/\sqrt{2}$  from the nanorod axis ( $r$  is the nanorod radius) in the direction of the closest  
421 nanorod. The dipole moment was set collinear to the  $z$  axis along the direction of the tunnelling current<sup>7</sup>.  
422 For treatment of the full 3D vectorial electromagnetic problem, finite element numerical simulations  
423 (COMSOL software package) were employed. To mimic the emission of the dipole in an infinite (in a  
424 lateral direction) metamaterial slab,  $6 \times 6$ ,  $8 \times 8$  and  $10 \times 10$  nanorod arrays were modelled, returning  
425 essentially the same results, which confirms the validity of the approach for the infinite array of  
426 nanorods. In all the models, the simulation domain was surrounded by perfectly matched layers,  
427 ensuring the absence of reflection from its boundaries.

428

429 **Data availability.** All the data supporting this research are presented in full in the results section and  
430 supplementary materials. The data that support the plots within this paper and other findings of this  
431 study are available from the corresponding author upon reasonable request.

432 **References**

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