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1 **Plasmo-electronic properties of self-assembled gold** 2 **nanoparticles: impedance spectroscopy experiments** 3 **combined with numerical simulations**

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9 **Abstract:** Plasmo-electronics is a fast developing field driven by the combination of
10 charge transport and surface plasmons in metal nanostructures. In this paper, we report
11 on theoretical and experimental investigations of the plasmoelectronic properties of
12 self-assembled monolayers of colloidal gold nanoparticles. A local plasmonic-
13 electronic nano-junction is introduced, as the fundamental component of a meso-scale
14 electrical network, and serves as the beginning point for the development of a multi-
15 scale modeling strategy. The Inter-particle charge tunneling and accumulation account
16 for the dynamical charge transport; the plasmonic properties are implemented at the
17 nanoscale using electro-dynamic calculations based on the discrete dipole
18 approximation (DDA) method. The electric characteristics of the macroscopic
19 nanoparticle network are calculated using a numerical resolution of the current-bias
20 equations based on Kirchhoff's laws. Disorder effects due to size and position
21 fluctuations of the nanoparticles within the network as well as dislocations and point
22 defects in their spatial arrangement are taken into account. The effects of light
23 excitation intensity and wavelength on the nano-junction photo-conductance and on
24 the macroscopic photo-resistance of the nanoparticle network are addressed. In
25 particular, plasmo-electronic conduction paths are extracted from the coupled DDA-
26 Kirchhoff numerical simulations and their statistical distribution is investigated as well
27 as their dependence on path length. The theoretical results are compared with
28 impedance spectroscopy measurements performed under optical excitation. We found
29 a good agreement between the predicted impedance Nyquist plots and resonance
30 properties, and the measurements. In particular, we were able to estimate the surface
31 plasmon assisted photo-electric conversion coefficient involving first neighbor
32 nanoparticles. We found that the photo-conductance of a single nano-junction formed
33 by a dimer of nearly touching nanoparticles is around $18 \text{ nS.W}^{-1}.\text{cm}^2$ under resonant
34 plasmonic excitation. The presented work provides insight into the photo-induced
35 charge transport in self-assembled nanoparticle networks and opens the route to novel
36 applications in the field of plasmo-electronics.

37

38 **1. Introduction**

39 The driving force behind the development of plasmoelectronics is the link between
40 charge transport and surface plasmons in metal nanostructures [1]–[5]. It has been
41 shown that charging metal nanoparticles can alter their plasmonic response, and vice
42 versa, that surface plasmon excitation of a nanoparticle assembly can modify

43 macroscopic fluxes of charges [6]–[8]. In particular, a rise or a decrease of
44 conductance, under optical excitation tuned to the nanoparticles surface plasmon
45 resonance, has been pointed out [6], [9], [10]. In this situation, it had been found that
46 negatively charged ligands act as charge traps lowering the free carrier density and
47 resulting in a negative photo-conductance. However, since positive photo-conductance
48 with charged ligands has also been discovered, this view has been vividly contested in
49 the literature [11]–[13]. Additionally, the ligand molecules' ability to impose a tunnel
50 barrier between two adjacent nanoparticles, regardless of their charge state, determines
51 whether the macroscopic electrical properties of the nanoparticle assemblies behave
52 like a metal or an insulator [14]. Moreover, despite the fact that these NPs assemblies
53 are granular in form, that is, made up of conductive and insulating regions, most
54 published investigations to date have concentrated on the analysis of the resistance
55 properties, only [6] [9]–[11], [13]–[21]. The capacitive properties have only been
56 briefly discussed in a few papers [12], [22]. In this respect, we have previously
57 demonstrated [12], that both resistive and capacitive characteristics are complementary
58 and can be used to further understanding the charge transport properties of self-
59 assembled nanoparticle networks. Indeed, the macroscopic electrical characteristics of
60 self-assembled NPs were experimentally investigated using impedance spectroscopy
61 and were modeled using a bottom-up approach in which local interconnected nano-
62 junction circuits are introduced as building blocks of a macroscopic electrical circuit
63 to describe the charge transport properties of the nanoparticle self-assembly (Figure
64 2). However, the photo-induced effects were accounted only at the macroscopic level,
65 which provided a first attempt to the modeling of the plasmonic induced photo-
66 conductance in self-assembled gold nanoparticle networks and the macroscopic
67 conversion efficiency of the electromagnetic energy into electric current has been
68 estimated.

69 In this paper, we focus on the conversion of light into electrical current in self-
70 assembled plasmonic NPs networks. This phenomenon is quite complex and involves
71 several interaction steps between elementary excitations (plasmons, electron-hole
72 pairs, phonons), but it is still poorly understood in terms of the relationship between
73 local opto-electronic properties at the nanoparticle scale and the macroscopic electrical
74 characteristics of the nanoparticle self-assembly. We demonstrate that utilizing
75 numerical simulations combined with impedance spectroscopy measurements, it is
76 possible to connect the macro-scopic and the nano-scopic opto-electronic properties of
77 metal NPs assemblies. To account for the photo-induced charge carriers generation
78 and transport, a local positive photoconductance is introduced at the nano-scale. The
79 current passing through the nanoparticle assembly, including its optical component, is
80 determined by implementing electrodynamic calculations into Kirchhoff's laws. This
81 method enables the definition of a macroscopic photo-conductance. The theoretical
82 results are discussed in terms of plasmoelectronic properties of the nanoparticle self-
83 assembly and are compared to impedance spectroscopy measurements carried out
84 under optical excitation of the plasmonic resonance of the nanoparticles. In this way
85 we are able to assess the efficiency of the plasmonic assisted light-to-current
86 conversion at the nanoscopic level. Such a physical quantity is very difficult to
87 determine including in near-field based optical spectroscopy techniques.

88

89 **2. Experimental and numerical details:**

90

91

2.1 - Chemical synthesis and sample preparation:

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The chemical synthesis procedure is described in details elsewhere [22], [23].

93

Briefly, gold nanoparticles stabilized with dodecanethiol (C_{12}) organic ligands (1.2nm

94

length) were synthesized with the protocol described by Zheng et al. [24]. The average

95

size of the nanoparticles is $7 \pm 0.7 \text{ nm}$ determined by transmission electronic

96

microscopy (TEM). On the other hand, interdigitated gold electrodes were patterned

97

on a $125 \mu\text{m}$ thick polyimide (Upilex) film using laser lithography and a 50 nm thick

98

Au layer was deposited over the entire surface by IBS-E ion beam sputtering. After

99

lift-off, a 1 mm^2 device consisting in 50 pairs of inter-digitated $5 \mu\text{m}$ wide electrodes

100

separated by $5 \mu\text{m}$ is obtained and connected to external gold electrodes (Figure 1a).

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Gold NPs from the colloidal solution were deposited on the device using the ethylene

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glycol drop casting method described elsewhere (Figure 1b) [22]. This technique

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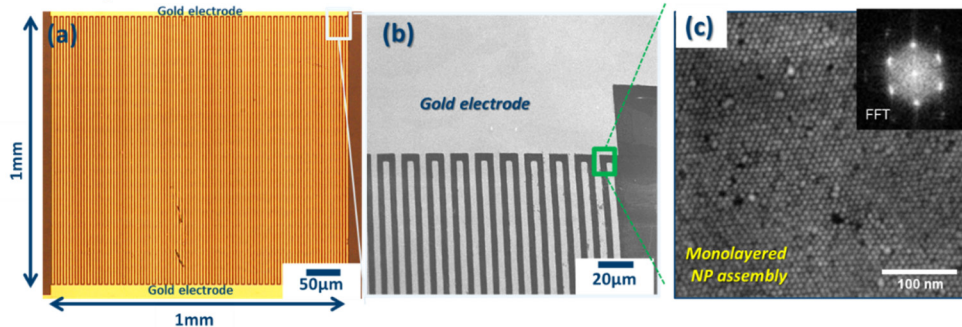
allows to obtain a quite uniform and homogeneous monolayer of self-assembled

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nanoparticles well ordered in a hexagonal lattice network on a macroscopic scale (1

105

mm^2) (Figure 1).



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107

Figure 1 : (a) Optical image showing a $1 \text{ mm} \times 1 \text{ mm}$ device formed by 50 interdigitated electrodes (b) Scanning electron

108

microscopy (SEM) image of the interdigitated electrodes on top of which the NP assembly is formed, (c) High

109

resolution SEM image of the active area showing a monolayer of 7 nm gold nanoparticles self-assembled in a hexagonal

110

lattice network, as attested by the electron diffraction pattern in the inset.

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112

113

Impedance spectroscopy measurements were performed at room temperature

114

using a Keysight impedance analyzer EA4990A, in the $20 \text{ Hz} - 5 \text{ MHz}$ frequency range

115

with a 500 mV AC voltage. The set-up is equipped with an optical fiber located above

116

the sample which allows to shine laser light on the 1 mm^2 entire active area (Figure 1a).

117

The optical fiber is connected to three laser diodes, operating at $\lambda = 405, 532$ and 640

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nm wavelengths and up to W/cm^2 intensity.

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120

121

The approach developed in this work is based on numerical simulations of the

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dynamical charge transport properties of a network composed of inter-connected

123

electric nano-circuits building blocks (Figure 2).

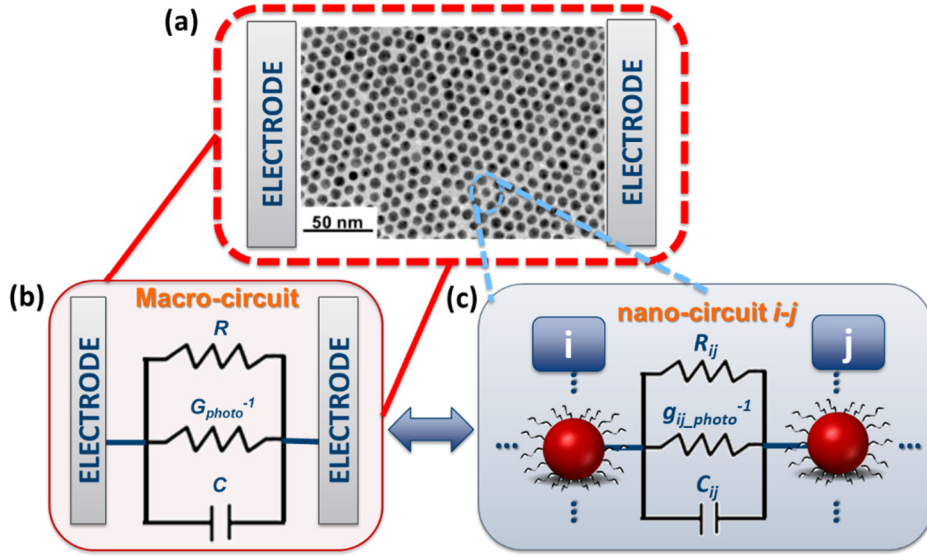


Figure 2: (a) Transmission Electron Microscopy image of a ca. 220nm x 150nm region of the NP assembly with schematic contact electrodes, (b) electrical circuit formed by parallel resistance R , capacitor C and photo-resistance G_{photo}^{-1} describing the charge transport across the network formed by the inter-connected nano-junctions (c). Each nano-junction, formed by a pair of first neighbor nanoparticles, consists in parallel inter-particle tunneling resistance R_{ij} , capacitor C_{ij} and photo-resistance $g_{ij_photo}^{-1}$.

Each nano-junction is an electrical connexion between first neighbor nanoparticles (labeled i and j) and consists in parallel inter-particle resistance R_{ij} , capacitor C_{ij} and photo-resistance $g_{ij_photo}^{-1}$ (Figure 2c). Calculations were performed for a single layer of spherical gold NPs. The sizes and positions of the nanoparticles, as well as the inter-particle gap distances were extracted from a 100 nm x 100 nm area of the transmission electron microscopy (TEM) images (Figure 2a). The histogram of interparticle distances in Figure ESI 1b shows that the average inter-particle gap separation is around 2.8 nm which is slightly larger than twice the dodecanethiol molecule length (1.2 nm). This indicates that disorder due to size and position fluctuations, to point defects (nanoparticle vacancies) and to dislocations and misfits in the nanoparticle network are present. Figure ESI 1a depicts the 100 nm x 100 nm nanoparticle region that serves as our model network for the computer simulations. In this way, the actual spatial arrangement of the nanoparticles are taken into account in the calculations and in the comparison with the experimental data.

Each (i,j) pair of nanoparticles located at positions (r_i, r_j) of the 2D network gives rise to a parallel electrical nano-junction (Figure 2c) with admittance:

$$Eq. 1 \quad \chi_{ij} = 1/R_{ij} + g_{ij_photo} + jC_{ij}\omega$$

As shown in previous works [11], [14], [25], the quantum tunnelling resistance R_{ij} between first neighbour nanoparticles is given by:

$$Eq. 2 \quad R_{ij} = R_0 \cdot e^{\xi(v_{ij}, T)}$$

where R_0 is the inter-particle tunnelling resistance at the touching limit, *i.e.* for vanishing inter-particle gap distance l_{ij} , ξ accounts for the charge tunnelling and for the Coulomb blockade effects and is given by ([11], [14], [25], [25]):

154 Eq. 3 $\xi = \beta l_{ij} - \ln(g(E_c, T, V_{ij}))$ with $g(E_c, T, V_{ij}) = \frac{1}{eV_{ij}} \left(-\frac{E_c - eV_{ij}}{1 - e^{(E_c - eV_{ij})/k_B T}} + \right.$
 155 $\left. \frac{E_c + eV_{ij}}{1 - e^{(E_c + eV_{ij})/k_B T}} \right)$

156 Where β is the tunnelling decay constant, E_c is the Coulomb charging energy, T the
 157 temperature and V_{ij} is the voltage between first neighbour nanoparticles i and j . In the
 158 following we use $\beta = 5 \text{ nm}^{-1}$ and $E_c = 50 \text{ meV}$ ([11], [13]) to describe the tunneling
 159 resistance in the absence of optical excitation.

160 It is worth noting that the bias voltage applied to the nanoparticle network is of the
 161 order of volts leading to inter-particle voltage V_{ij} very small compared to $E_c/e \sim 50 \text{ mV}$.
 162 In addition $E_c > k_B T$ at room temperature. Using these two statements, Eq. 3 can be
 163 approximated by [27]:

164 Eq. 4
$$\xi \approx \beta l_{ij} + E_c/k_B T$$

165 Assuming spherical nanoparticles, the inter-particle capacitor C_{ij} is given by [22],
 166 [26]:

167 Eq. 5
$$C_{ij} = \pi \varepsilon \bar{d}_{ij} \ln(1 + \bar{d}_{ij}/l_{ij})$$

168 Where $\bar{d}_{ij} = (d_i + d_j)/2$ is the mean diameter of the i and j nanoparticles and ε is
 169 the permittivity of the surrounding medium (*i.e.* of the ligand molecules in our case).

170 As shown experimentally by Mangold *et al.* [10], [17], Gauvin *et al.* [28], the
 171 macroscopic photo-conductance increases linearly with increasing laser intensity for
 172 low laser irradiation (below 7 kW/cm^2). This is confirmed in our investigated
 173 nanoparticle networks as shown in Figure ESI 2. Based on this experimental finding,
 174 we introduce a local nanoscopic photoconductance:

175 Eq. 6
$$g_{ij_photo}(\lambda) = k_{ij}(\lambda) \cdot I_{ij}(\lambda) \cdot e^{-E_c/k_B T}$$

176 Where $k_{ij}(\lambda)$ is a wavelength dependent local photo-conductance efficiency involving
 177 first neighbor nanoparticles and the surrounding ligands molecules. $I_{ij}(\lambda) =$
 178 $F_{ij}^2(\lambda) I_0$ is the local light intensity and $F_{ij}(\lambda) = |E_{ij}(\lambda)/E_0|$ is the electric field
 179 enhancement factor which accounts for the plasmonic resonance; $I_0 = |E_0|^2$ is the
 180 incident optical intensity.

181 In our approach, the light-to-current conversion mechanism is treated globally,
 182 *i.e.* as due to both the nanoparticle and its surrounding medium; indeed, the ligand
 183 molecules may also absorb light through HOMO-to-LUMO transitions and may thus
 184 participate to the photo-generation of electron-hole pairs. Therefore, we assume that
 185 $F_{ij}(\lambda)$ is the electric field enhancement factor in the gap region between i and j
 186 nanoparticles. The photo-generated charges flow across the nanoparticle network
 187 owing to quantum tunneling between first neighbor nanoparticles. The photo-
 188 conductance efficiency $k_{ij}(\lambda)$ depends on the optical wavelength because the tunneling
 189 process involves high energy photo-excited states (see Figure ESI 3), the so-called hot
 190 charge carriers. Therefore, we make the assumption that $k_{ij}(\lambda)$ takes the form :

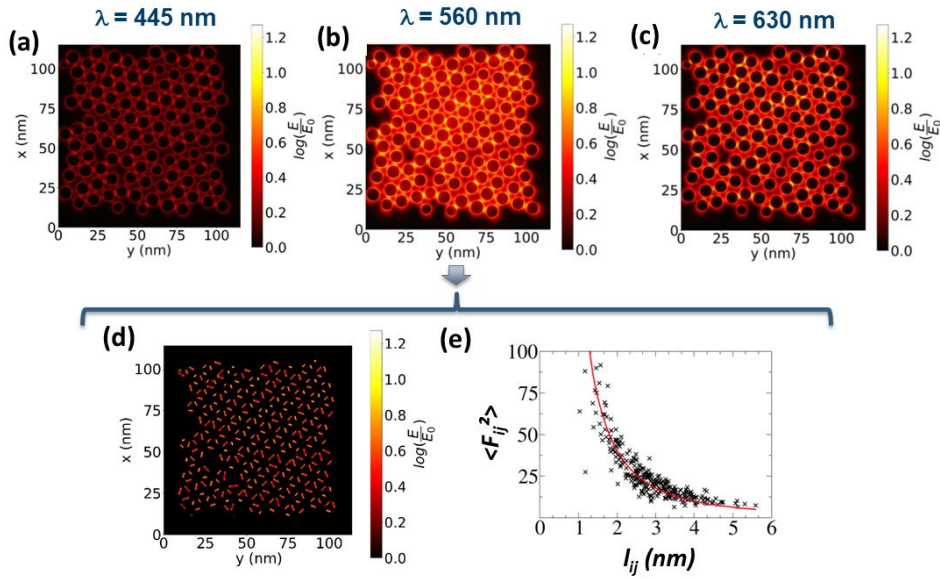
191 Eq. 7
$$k_{ij}(\lambda) = k_0(\lambda) \cdot e^{-\beta(\lambda) \cdot l_{ij}}$$

192 Where $k_0(\lambda)$ is a wavelength-dependent photo-conductance efficiency in
 193 Siemens per unit of light intensity, which accounts for the photo-generation charge
 194 carriers at vanishing gap distance between two nanoparticles; and the exponential term
 195 describes their interparticle tunneling; $\beta_{hot}(\lambda) = \sqrt{2 \cdot m \cdot (V_b - E(\lambda))/\hbar}$ is the wave
 196 vector of the photo-generated hot electrons, in which, $m = 0.28 \cdot m_0$ is the carriers

197 electron effective mass [29], $E(\lambda)$ is the photon energy and $V_b = 4.16$ eV is the energy
 198 barrier height [29]. For example, at $\lambda = 532$ nm, $\beta_{hot} = 3.66$ nm⁻¹ and is smaller than
 199 $\beta = 5$ nm⁻¹ which conveys the idea that hot carriers can tunnel over larger distances
 200 than thermalized carriers (Figure ESI 3).

201 Calculations based on the Discrete Dipole Approximation (DDA) [30], [31]
 202 were performed in order to determine the plasmonic field enhancement $F_{ij}(\lambda)$. The
 203 nanoparticle self-assembly model is the 100 nm x 100 nm area shown in Figure ESI 1a.
 204 The medium surrounding each nanoparticle is dodecanethiol (with optical index
 205 $n=1.46$).

206 Figure 3 shows maps of $F_{ij}(\lambda)$ calculated at three optical excitation wavelengths
 207 around the plasmonic resonance. These maps show that the electro-magnetic
 208 interactions between the NPs give rise to plasmonic hot spots in the gap regions
 209 between the nanoparticles. For the calculation of the local field intensity in Eq. 6, we
 210 consider the intensity enhancement $\langle F_{ij}^2(\lambda) \rangle$ averaged over the gap distance between
 211 first neighbor nanoparticles (Figure 3d). $\langle F_{ij}^2(\lambda) \rangle$ is around two orders of magnitudes
 212 for a 1 nm interparticle distance and decreases with increasing l_{ij} (Figure 3e) which
 213 confirm the origin of the plasmonic resonance as due to the near-field interaction
 214 between first neighbor nanoparticles.



215 Figure 3 : Electric field intensity enhancement $F_{ij}(\lambda) = |E_{ij}(\lambda)/E_0|$ calculated using
 216 DDA simulations performed on a 100 nm x 100 nm nanoparticle assembly shown in
 217 Figure ESI 1a. Maps of F_{ij}^2 calculated around the surface plasmon resonance at 445
 218 nm (a), 560 nm (b) and 630 nm (c). The excitation wave is circularly polarized in the
 219 assembly plane, (d) Map of $\langle F_{ij}^2 \rangle$ the field intensity enhancement calculated at 560
 220 nm and averaged over the gap distance between each pair of nanoparticles; (e) plot of
 221 $\langle F_{ij}^2 \rangle$ as a function of inter-particle distance l_{ij} .
 222

223 The $\langle F_{ij}^2 \rangle$ calculated using the DDA numerical simulations are used in Eq. 6 to
 224 generate the local photoconductances.
 225

226 The complex admittance matrix $[Y]$ of the electrical network, formed by the
 227 interconnected nano-junctions, is constructed assuming that all first neighbor
 228 nanoparticles are located within a ring centered on the considered nanoparticle. The
 229 current flowing throughout the NP network is computed according to Kirchhoff's laws
 230 and by solving numerically the matrix equation[32]:

231 Eq. 8
$$[V(\omega)] = [Y(\omega)]^{-1}[I(\omega)]$$

232 where $[V(\omega)]$ and $[I(\omega)]$ are, respectively, the voltage and the injected current
 233 vectors, and $[Y(\omega)]$ is the complex admittance matrix of which non-diagonal and
 234 diagonal terms are, respectively, $Y_{ij}(\omega) = -\chi_{ij}(\omega)$ for $i \neq j$ and $Y_{ii}(\omega) = \sum_j \chi_{ij}(\omega)$; the
 235 latter being the total admittance connected to node i [33].

236 The overall admittance of the network is $Y_0^{-1}(\omega) = V_0(\omega)/I_0(\omega)$ where $V_0(\omega)$ is
 237 the voltage vector at the collecting electrode and $I_0(\omega)$ is the injected current vector.

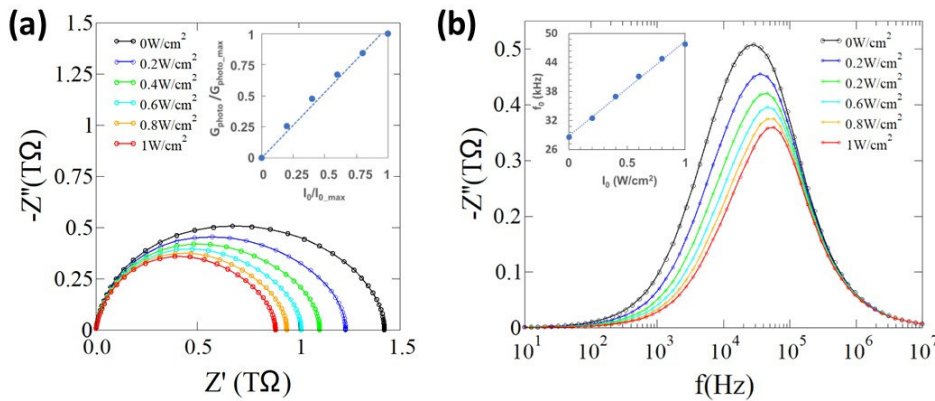
238 It is important to note that after the admittance $\chi_{ij}(\omega)$ (Eq. 1) of the local
 239 nano-junction is adjusted for the local photo-conductance $g_{ij_photo}(\lambda)$ (Eq. 6),
 240 calculated using DDA simulations, and the matrix equation (Eq. 8) is numerically
 241 solved using Kirchhoff's laws, one obtains the overall conductance, capacitance, and
 242 photo-conductance of the nanoparticle assembly. The numerical simulations utilizing
 243 this strategy enable modeling of the plasmoelectronic properties of self-assembled
 244 metal nanoparticles and is, going forward, referred to as DDA-Kirchhoff's method.
 245

246 4. Results and discussion:

247 4.1 Numerical simulations:

249 Figure 4 presents Nyquist plots (Figure 4a) and resonance curves of the
 250 imaginary part $-Z''(\omega)$ of the impedance calculated using DDA-Kirchhoff
 251 simulations. The parameters used in these simulations are $R_0 = 80$ k Ω (in Eq. 2) and
 252 $k_0 = 18$ nS.W $^{-1}$.cm 2 (in Eq. 7). The choice of these values will be discussed later.

253 All Nyquist plots have nearly a semicircle shape which is a characteristic
 254 feature of an equivalent circuit consisting in parallel resistance R , capacitor C and
 255 photo-resistance G_{photo}^{-1} .



256
 257
 258
 259
 260
 261
 Figure 4 : DDA-Kirchhoff numerical calculations of the impedance of the network shown in Figure ESI 1a. (a) impedance Nyquist plots in the range 20 Hz-1 MHz, without and with optical excitation at 532 nm with intensity increasing from 0 to 1W/cm 2 (inset: normalized photoconductance as a function of normalized I_0). (b) Spectrum of the Imaginary part of the calculated impedance $-Z''(\omega)$ (inset: corresponding f_0 evolution as a function of laser intensity).

262 The frequency dependence of the impedance arises from the capacitance
 263 contribution only. At this step, R , C and G_{photo}^{-1} can be considered as mesoscopic
 264 quantities reflecting the electric and plasmo-electric properties of the 100 nm x 100
 265 nm simulated network (Figure ESI 1a) formed by the interconnected nano-junctions.
 266 They are not macroscopic quantities yet, since the latter are related to the macroscopic
 267 properties of the samples (Figure 1) onto which impedance spectroscopy
 268 measurements were performed (see discussion below).

269 First, a clear decrease of the impedance with increasing intensity of the optical
 270 excitation can be observed in Figure 4a. This can be understood in terms of the
 271 equivalent circuit impedance $\frac{R}{1+RG_{photo}}$ formed by the parallel resistance and photo-
 272 resistance G_{photo}^{-1} in the low-frequency limit (values of $Z'(\omega)$ on the horizontal axis
 273 of Nyquist plots in Figure 4a). Nyquist plot calculated without light irradiation
 274 ($G_{photo} = 0$), gives $R = 1.4 T\Omega$. With increasing optical excitation, G_{photo} increases
 275 and may dominate the resistive character of the circuit in the limit of strong irradiation
 276 intensity ($G_{photo} \gg R$). The inset of Figure 4a shows the values of G_{photo} deduced
 277 from the low-frequency limit of the Nyquist plots (Figure 4a).

278 Inset of Figure 4a shows that G_{photo} increases linearly from 0 to *c.a.* 0.4 pS
 279 with irradiation intensity I_0 in agreement with the local photo-conductance model (Eq.
 280 6) implemented at the nanoscale and with the experimental data (Figure ESI 2).
 281 Moreover, one can notice in Figure 4 that the Nyquist plots are not perfect semi-circles;
 282 they are depressed, *i.e.* the ratio between the maximum values of the imaginary and
 283 real parts of the impedance $-Z''_{max}/Z'_{max} < 0.5$. For instance, without optical
 284 excitation (black dots in Figure 4a) $-\frac{Z''_{max}}{Z'_{max}} = 0.36$ This depressed feature suggests
 285 that the equivalent circuit is formed by a distribution of parallel resistance and
 286 capacitor circuits rather than being defined by a single circuit. Such a distribution is
 287 generated by the disorder due to size and position fluctuations of the nanoparticles and
 288 also to point defects and dislocations present in the assembly network (Figure 2a and
 289 Figure ESI 1a). Indeed, as shown in Figure ESI 4, for a perfectly ordered hexagonal
 290 arrangement of the nanoparticles, the calculated Nyquist plot is a perfect semi-circle.
 291 When 15% random fluctuations of the nanoparticle size and position are introduced,
 292 all the Nyquist plots calculated for the different random guesses, are not only depressed
 293 but their shape clearly deviates from a semi-circle (Figure ESI 4). This occurs because
 294 of the fluctuations of the local inter-particle tunneling resistance R_{ij} , capacitor C_{ij} and
 295 photo-conductance g_{ij_photo} which lead to statistical distributions of relaxation times
 296 $\tau_{ij} = \frac{R_{ij}C_{ij}}{1+R_{ij}g_{ij_photo}}$. As a matter of fact, in a perfectly ordered network, the interparticle
 297 separation l_{ij} and hence R_{ij} , C_{ij} and $g_{ij_photo}^{-1}$ are well defined, thus leading to a
 298 unique relaxation time τ_{ij} (Figure ESI 5b).

299 Figure 4b shows the imaginary part $-Z''$ of the impedance as a function of
 300 frequency. Each spectrum consists of a resonance peak. Assuming a perfectly ordered
 301 network, the $-Z''(\omega)$ resonance peak has a Lorentzian line shape (corresponding to a
 302 single relaxation time) and the resonance frequency is given by $f_0 = \frac{1}{2\pi RC}$; at the nano-
 303 junction scale f_0 is determined by the interparticle tunnelling resistance (Eq. 2) and
 304 capacitor (Eq. 5). In the numerical simulations, the tunnelling parameter $R_0 =$

305 $80\text{ k}\Omega$ has been chosen in such a way that the resonance frequency $f_0 = 28\text{ kHz}$
 306 corresponds to the one observed experimentally (see discussion below), without
 307 optical excitation, which leads to $R = 1.4\text{ T}\Omega$ and $C = 4aF$. This latter value is the
 308 equivalent capacitor of all serie and parallel nano-junctions forming the electrical
 309 network (C_{ij} being given by Eq. 5). The large value of R and the small value of C are
 310 consistent with the small size of the model nanoparticle network (100 nm x 100 nm).
 311 Under optical illumination, the resonance frequency increases with increasing light
 312 intensity (inset of Figure 4b). As a matter of fact, the resonance frequency of the
 313 equivalent circuit shown in Figure 1b is given by:

314 Eq. 9
$$f_0 = \frac{1+RG_{photo}}{2\pi RC}$$

315 Hence, when G_{photo} increases, the resistive component of the equivalent
 316 circuit decreases and the resonance frequency increases linearly with irradiation
 317 intensity (inset of Figure 4b) in agreement with Eq. 6. The maximum of the resonance
 318 peak also decreases for the same reason.

319 It is worth to underline that the line shape of the $-Z''(\omega)$ resonance peaks in
 320 Figure 4b is not described by a Lorentzian function. Indeed, because of the disorder
 321 effects discussed above, the resonance peaks in Figure 4b are inhomogenously
 322 broadened according to the statistical distributions of the local relaxation time τ_{ij} . To
 323 confirm this point, we have calculated analytically the impedance Nyquist plot and
 324 resonance peak starting from the distribution of the relaxation times of the model
 325 nanoparticle network shown in Figure ESI 5. The depressed feature of the Nyquist plot
 326 and the non Lorentzian shape of $-Z''$ resonance are well reproduced thus confirming
 327 the role of disorder (Figure ESI 5).
 328

329 4.2 Plasmoelectronic conduction paths:

330
 331 For a full understanding of the optical excitation effect on the charge transport
 332 properties, it is interesting to exploit the numerical simulations in order to investigate
 333 the conduction paths supported by the nanoparticle network. The length of a
 334 conducting path and its electric characteristics are extracted from the numerical
 335 simulations as follows: first, the spatial distribution of all the nano-junctions formed
 336 by each pair of first neighbor nanoparticles is constructed according to the positions of
 337 the nanoparticles within the network. Second, only paths connecting the injection and
 338 the collection electrodes are selected. These percolating paths are the ones directly
 339 involved in the impedance spectroscopy measurements. Then, the length L_k of each
 340 individual k-path is calculated by summing the nano-junctions impedance. Its
 341 admittance is given by:

342 Eq. 10 :
$$Y_k = \frac{\prod_{n=1}^m \chi_{ij,n}}{\sum_{n=1}^m \prod_{p=1, n \neq p}^m \chi_{ij,p}}$$

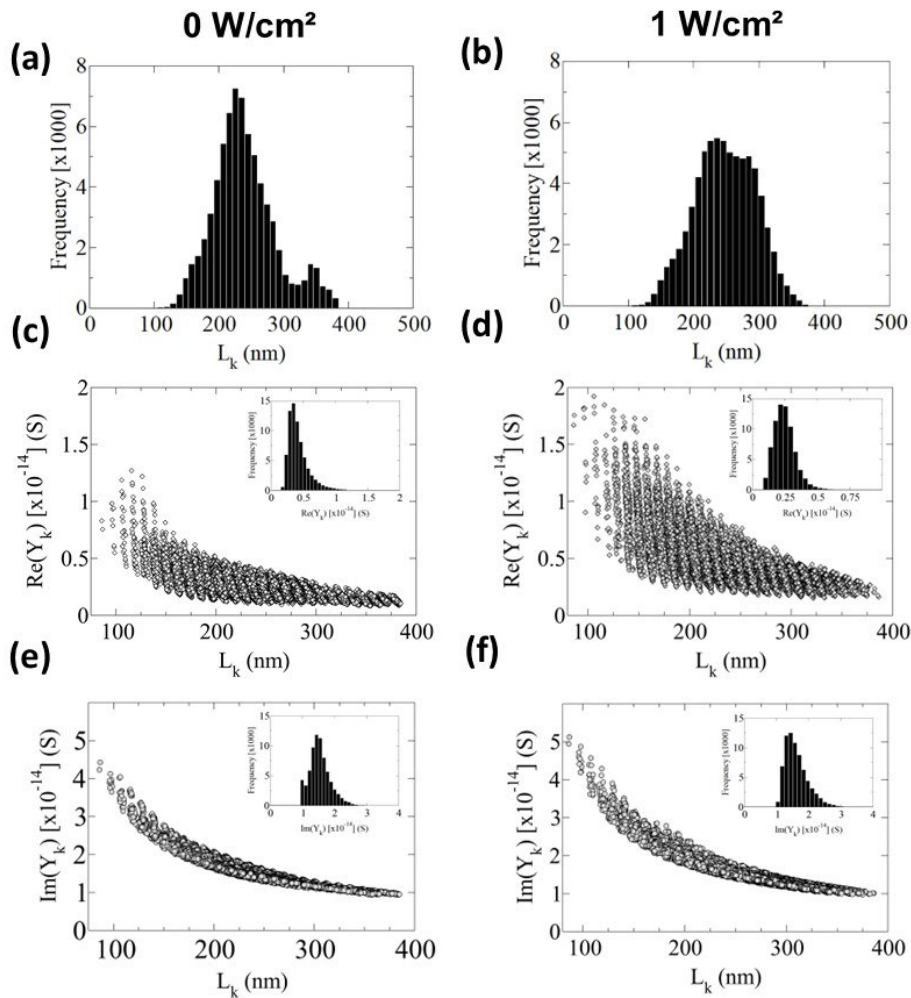
343 where m is the number of nano-junctions along the k-path and χ_{ij} is a nano-junction
 344 admittance (Eq. 1).

345 Figure 5 displays path length histograms calculated at the resonance frequency
 346 $f_0 = 28\text{ kHz}$ of the nanoparticle network. Without optical excitation, the path length
 347 histogram is bimodal with a main maximum around 220 nm, *i.e.*, nearly twice the inter-
 348 electrode separation and a secondary maximum at longer paths between 300 and 400
 349 nm. Under optical excitation at 1 W/cm^2 , the distribution of path lengths is more

350 uniform: the path length histogram is Gaussian like centered around 250 nm with 100
351 nm half width at half maximum. The optical excitation has the effect of condensing
352 the conduction path lengths around a mean value. This is related to the fact that the
353 photo-resistance (Eq. 6) due to the hot charge carriers is less sensitive to disorder
354 effects (*i.e.* to nanoparticle size and position fluctuations) than the resistance associated
355 with thermalized charge carriers (see Figure ESI 6).

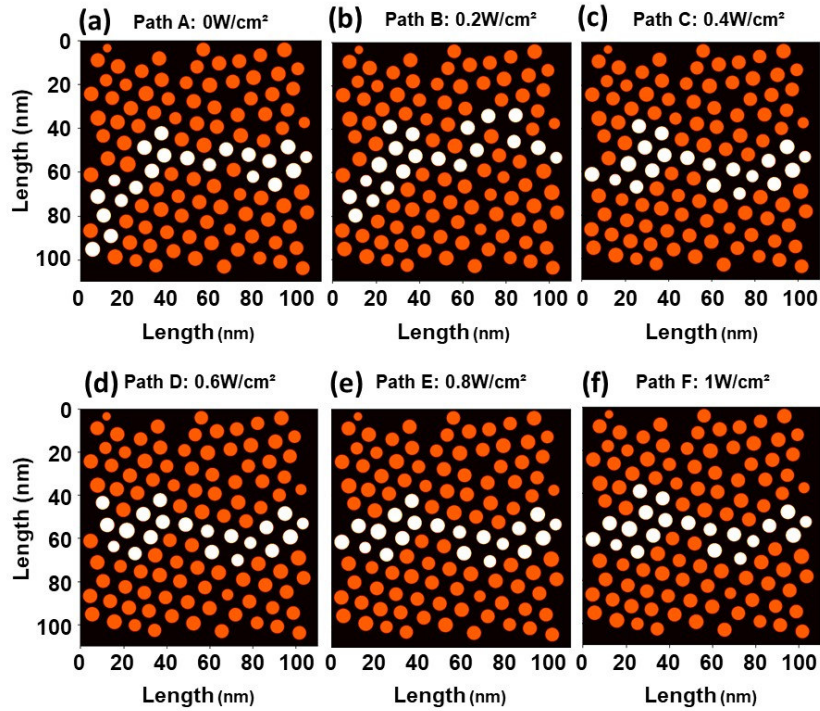
356 Figure 5 c-f depict the real (conductance) and imaginary (susceptance) parts of
357 path admittance as a function of path length calculated at the resonance frequency. For
358 a given path length, the values of the admittance are scattered over a wide range (Figure
359 5 c-f) which means that paths of the same length may have very different electrical
360 characteristics. This is particularly visible in the conductance (Figure 5c, d) because
361 the tunnelling resistance varies exponentially with the inter-particle distance (Eq. 2)
362 and is therefore very sensitive to fluctuations of the size and position of a nanoparticle
363 within the network. The susceptance of the nanoparticle network (Figure 5e, f) is less
364 sensitive to disorder effects because of the weaker logarithmic dependence of the local
365 capacitors (Eq. 5) on the interparticle distance.

366 As shown in Figure 5c, d path admittance is enhanced by the optical excitation
367 in agreement with Nyquist plots (Figure 4); as a consequence, for a given path length,
368 the conductance and susceptance are scattered over a wider range (compared to Figure
369 5 e, f). The optical excitation has a strong impact on the conductance since the local
370 photo-conductance introduced in Eq. 6 is purely real. For this same reason, we might
371 have expected no influence on the susceptance. However, since the complex
372 admittance combines both resistive and capacitive contributions (Eq. 10), its
373 susceptance component depends not only on the local interparticle resistance R_{ij} and
374 local interparticle capacitor C_{ij} , but also on the local photo-resistance $g_{ij_photo}^{-1}$. That's
375 why the susceptance of the nanoparticle network is also modified by the optical
376 excitation. The path admittance is strongly influenced by disorder as shown by the
377 scattered values of conductance and capacitance (Figure 5c-f) and decreases roughly
378 as the inverse path length. They are strictly proportional to the inverse path length only
379 in the case of a perfectly ordered network as shown in previous works [34].



380 Figure 5 : (a,b) histograms of conduction path lengths extracted from the DDA-Kirchhoff numerical simulations of the
 381 TEM nanoparticle network shown in Figure ESI 1a. Calculations were performed at the resonance frequency $f_0=28$
 382 kHz, without and with optical excitation at 560 nm wavelength and 1 W/cm^2 intensity. (c, d) path conductance as a
 383 function of path length L_k . (e, f) path susceptance as a function of path length L_k . The insets in c-f show conductance
 384 (c,d) and susceptance (e-f) histograms.
 385

386 Moreover, Figure 5 c-f display the conductance and susceptance histograms
 387 calculated with and without optical excitation. The histograms follow a log-normal
 388 distribution, as shown in a previous study [34], which indicates that conductance and
 389 susceptance indeed result from the sum of the numerous small independent local
 390 interparticle impedances along the conducting paths.



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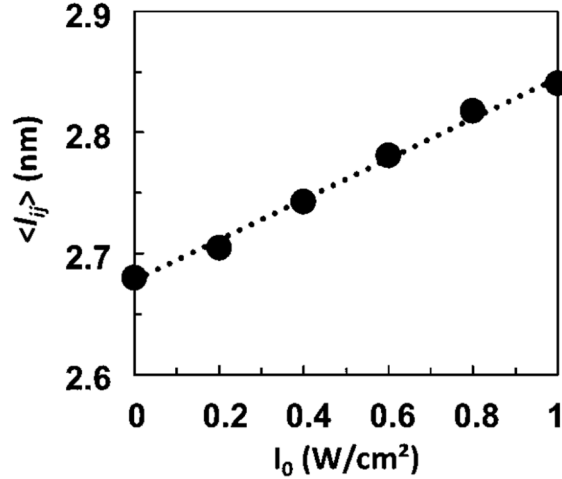
Figure 6 : Plasmo-electronic conduction paths. (a) Conduction path A is calculated without optical excitation. (b, c and d) Paths B, C and D are calculated with optical excitation at 532 nm and intensity from 0 to 1 W/cm². Each path module admittance $|Y_k|$ is in the range $[1.8 \times 10^{-14} \text{ S} - 2 \times 10^{-14} \text{ S}]$. The path length decreases from 200 nm for path A to 197 nm for path F.

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DDA-Kirchhoff numerical simulations allow to visualize the conduction paths and the changes induced by the optical excitation. To do so, we have selected conduction paths with nearly the same conductance c.a. $2 \cdot 10^{-14} \text{ S}$ and comparable length around 200 nm, *i.e.*, twice the network size and inter-electrodes separation. In this way, when the optical excitation is applied, only the relative contribution of the resistance and photo-resistance, along the path, is modified; its overall conductance being nearly constant. Figure 6 displays such conduction paths without (path labeled A) and with (paths labeled B-F) optical excitation. Without optical excitation, path A involves 21 nano-particles and the average distance between the involved first neighbor nanoparticles is 2.68 nm. With optical excitation at a moderate intensity of 0.2 W/cm^2 , path B is 198 nm long and involves 20 nanoparticles with a slightly larger average interparticle distance of 2.70 nm. When the optical excitation is increased to 0.4 W/cm^2 , path C involves 20 nanoparticles with an average distance of 2.74 nm. With further increase from 0.6 to 1 W/cm^2 , the length of path D, E and F are *c.a.* 197 nm and involves 20 nanoparticles with increasing average distances from 2.78 to 2.84 nm (see Figure 7). The variation of the relative admittance $\Delta Y_k = (|Y_k| - |Y_{k|\text{dark}}|) / |Y_{k|\text{dark}}|$ of the conduction paths shown in Figure 6 is less than 5% which ensures the fact that we are comparing conduction paths with very similar admittance.

It appears that the effect of the optical excitation is to reduce the path length and correlatively increase the average distance $\langle l_{ij} \rangle$ between first neighbor

417 nanoparticles for a given path admittance. We found that $\langle l_{ij} \rangle$ increases by *c.a.* 0.16
 418 nm per unit of optical excitation intensity (in W^{-1}cm^2) as shown in Figure 7.



419
 420 *Figure 7: Average distance $\langle l_{ij} \rangle$ between first neighbor nanoparticles involved in the plasmo-electronic conduction*
 421 *paths (A to F of Figure 6) as a function of laser intensity I_0 . The dotted line shows a linear least-square fit.*
 422

423 This effect can be understood in terms of optical generation of hot carrier's.
 424 Indeed, according to the local photo-conductivity (Eq. 6 and Eq. 7), the photo-excited
 425 hot carriers can tunnel over larger distances ($\beta^{-1} = 0.27 \text{ nm}$) than thermalized
 426 carriers ($\beta^{-1} = 0.2 \text{ nm}$). Therefore, under optical excitation a smaller number of
 427 nanoparticles is required for a conduction path with the same conductance compared
 428 to the situation without optical excitation. This underlines the role of the plasmonic
 429 resonance in terms of not only enhancement of the local optical field (Figure 3), but
 430 also of photo-generation of hot carriers. This latter effect is at the origin of the different
 431 optical conduction paths displayed in Figure 6 which we may call plasmo-electronic
 432 conduction paths.

433 434 **4.3 Comparison between DDA-Kirchhoff simulations and experiments:**

435 One must scale-up the dimensions of the simulated nanoparticle network to the
 436 macroscopic scale in order to compare numerical simulations with impedance
 437 spectroscopy data, quantitatively. However, numerical simulations of the charge
 438 transport properties of a macroscopic nanoparticle network require a significant
 439 amount of computation time and memory resources. To overcome this difficulty we
 440 use a simple rescaling method: the 100 nm x 100 nm simulated network (Figure 1) is
 441 replicated N_i times in series and N_j times in parallel; N_i and N_j are determined,
 442 respectively, by the distance between the interdigitated electrodes (Figure 1) and by
 443 their length. Additionally, a series contact resistance R_S can be added to take into
 444 account imperfections in the electrical connexion between the electrodes and the
 445 nanoparticle network. Then, the macroscopic impedance is calculated simply as

446 *Eq. 11*
$$Z_{macro}(\omega) = R_S + \frac{1}{N_e} \cdot \frac{N_i}{N_j} \cdot Z(\omega)$$

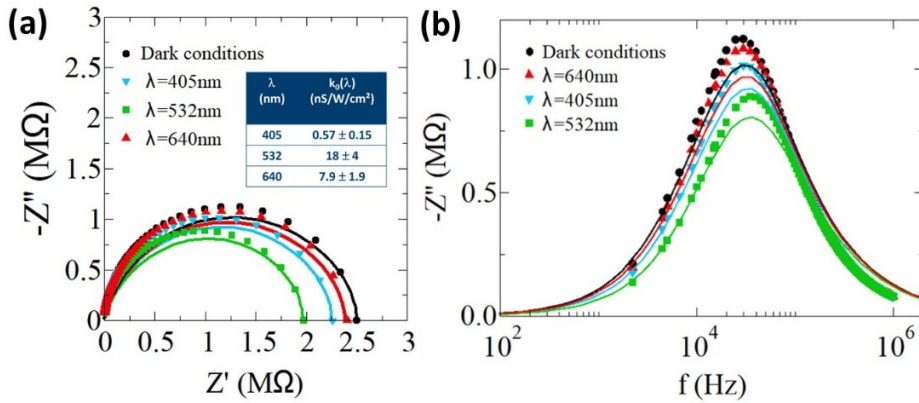
447 where $Z(\omega)$ is the mesoscale impedance of the 100 nm x 100 nm nanoparticle
 448 network calculated by DDA-Kirchhoff numerical simulations (Figure 3) and N_e is the

449 number of interdigitated electrodes (Figure 1). In our device $N_i=50$; $N_j=10000$ and
 450 $N_e=50$.

451 At high frequencies, the resistance of the nanoparticle network is shorted by its
 452 capacitance and only the series resistance R_s remains and can be estimated from the
 453 experimental data. We found $R_s \leq 1k\Omega$ from the impedance measured at the highest
 454 reachable frequency (10 MHz in our case). It is worth to underline that, according to
 455 Eq. 11, $-Z''_{macro}(\omega)$ and $-Z''(\omega)$ peaks exhibit the same resonance frequency f_0 and
 456 line shape; they differ only in their magnitudes by the scaling factor $\frac{1}{N_e} \cdot \frac{N_i}{N_j}$. The

457 straightforward rescaling method (Eq. 11) assumes that the size of the mesoscale
 458 network is large enough to capture all the structural features of the nanoparticle
 459 network, *i.e.*, the spatial arrangement of the nanoparticles including fluctuations of
 460 their sizes and positions as well as the presence of point defects and dislocations.

461 Figure 8 presents a comparison between the results of DDA-Kirchhoff's
 462 numerical simulations and impedance spectroscopy data.



463 Figure 8 : (a) Comparison between measured and calculated (full lines) impedance Nyquist's plots without and with
 464 optical excitation at $\lambda = 405, 532, 640$ nm and 0.36 W/cm² intensity (b) corresponding spectra of $-Z''(\omega)$; the table
 465 inserted in (a) shows the values of the $k_0(\lambda)$ factor in Eq. 6 used as a fitting parameter of the simulated Nyquist plots
 466 to the measured ones.

467 In the numerical simulations there are two adjustable parameters: the
 468 interparticle tunneling resistance R_0 in Eq. 2 and the charge carrier photo-generation
 469 efficiency k_0 in Eq. 7 when the optical excitation is used. As mentioned above, $R_0 =$
 470 80 k Ω has been determined in such a way that the calculated resonance frequency $f_0 =$
 471 28 kHz coincides with the one observed in the impedance spectroscopy
 472 measurements. Using this value of R_0 and the rescaling method described above one
 473 obtains the macroscopic values $R \sim 140M\Omega$ and $C \sim 0.04pF$. At this point one expects
 474 a good matching between the rescaled impedance (Eq. 11) and the measured one.
 475 However, we found that the calculations overestimate the measured impedance. The
 476 latter is of the order of 2.5 M Ω as can be seen on the Nyquist's plot (horizontal axis of
 477 Figure 8). The origin of this discrepancy lies in three main points:

478 First, the mesoscale network is assumed to be representative of the entire
 479 macroscopic network. However, Figure ESI 4 shows that for a 100 nm x 100 nm
 480 network with a hexagonal arrangement of the nanoparticles in which 15% size and
 481 position fluctuations are included, the impedance may vary up to a factor 20 depending
 482 on the network selected by the random guess (only a factor 4 is presented in Figure
 483 ESI 4).

484 Second, we found that depending on the filtering parameters used in the software
485 assisted filtering of the TEM image (Figure ESI 1a), the estimated nanoparticle size
486 position may vary by 5%. This variation, combined with the strong sensitivity of the
487 tunneling resistance to the inter-particle distance (Eq. 2), leads to an uncertainty on the
488 calculated network impedance that may also reach an order of magnitude. Moreover,
489 the parameters β and E_C determine the interparticle tunneling resistance (Eq. 2) and
490 may be affected by conformational changes of the ligand molecules which in turn may
491 have a strong impact on the overall macroscopic resistance.

492 Third, we did not take into account a possible effect of humidity from the
493 environment that would modify the conformation of the ligand molecules and thus the
494 permittivity of the medium surrounding the nanoparticles.

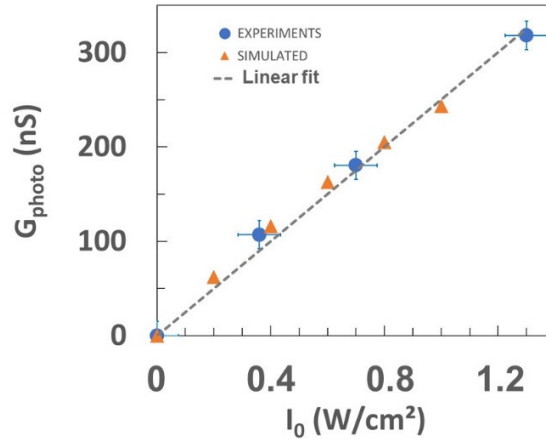
495 For these reasons, the calculated and measured impedances are significantly
496 different in magnitudes. However, the shape of the calculated and measured Nyquist
497 diagrams and resonance peaks can be compared once their amplitudes adjusted. To do
498 that, the calculated low-frequency impedance is fitted to the measured one, in the
499 absence of optical excitation. This corresponds to the (black) dot on the right side
500 (horizontal axis) of the Nyquist plot in Figure 8a. As shown in Figure 8, the Nyquist
501 plot, measured without optical excitation, is depressed $-Z''_{max}/Z'_{max} \sim 0.4$ (Figure
502 8a and Figure ESI 6) and the resonance peak of $-Z''(\omega)$ has a non-lorentzian shape
503 characterized by a low-frequency asymmetry. The calculations (full lines in Figure 8)
504 well account for these two features which are correlated and reflect the disorder effects
505 discussed in Figure 4. In fact, the measured and calculated linewidths of the resonance
506 peaks in Figure 8b are comparable, hence indicating that the variations in the size and
507 location of the nanoparticles and the networks defects (disorientations, dislocations...)
508 (Figure 1) are quite representative of the disorder present at the macroscopic scale.

509 Let's now focus on the effect of the optical excitation. As shown in Figure 8, the
510 nanoparticle assembly has been excited at 405, 532 and 640 nm wavelengths with 0.36
511 W/cm² laser intensity. The reduction in the radius of the Nyquist plots in Figure 8a and
512 in the amplitude of the resonance peaks in Figure 8b demonstrate that, after optical
513 excitation, the measured impedance of the nanoparticle network is lowered due to a
514 photo-conductance contribution in agreement with the simulation results presented in
515 Figure 4. Remarkably, the largest photo-induced effect is observed for $\lambda = 532$ nm
516 (green dots in Figure 8a), *i.e.*, close to the plasmon resonance of the nanoparticle
517 network (Figure 2) which underlines the plasmo-electronic character of the photo-
518 conductance.

519 DDA-Kirchhoff numerical simulations of the photo-induced plasmo-
520 electronic effect were then performed using the photo-current factor $k_0(\lambda)$ in Eq. 7 as
521 an adjustable parameter. The agreement between the calculated and measured
522 impedance Nyquist plots and resonance peaks, under optical excitation, is satisfactory.
523 In particular, the depressed character (Figure 8a) of the Nyquist plots and the linewidth
524 of the resonance peaks (Figure 8b) are well reproduced. The $k_0(\lambda)$ best-fit values are
525 quoted in Figure 8b. Close to the plasmonic resonance the photo-current conversion
526 factor is estimated at $k_0(532nm) = 18 \pm 4 \text{ nS} \cdot \text{W}^{-1} \cdot \text{cm}^2$ which means that at 0.36
527 W/cm², for nearly touching particles, the inter-particle photo-conductance is around 50
528 nS.

529 It is worth to underline that using the values of the nanoscopic photo-
530 conductance efficiency $k_0(\lambda)$ quoted in Figure 8a, the DDA-Kirchhoff numerical

531 simulations are able to account for the measured macroscopic photo-conductance as a
 532 function of both the optical excitation wavelength (Figure 8) and intensity (Figure 9).
 533 Close to the plasmonic resonance ($\lambda = 532\text{nm}$), we found that the macroscopic photo-
 534 conductance efficiency is $250 \pm 40 \text{ nS.W}^{-1}.\text{cm}^2$.
 535



536
 537 *Figure 9 : Calculated (triangles) and measured (dots) macroscopic photoconductance G_{photo} as a function of laser*
 538 *intensity I_0 at the plasmonic resonance ($\lambda=532\text{nm}$). The experimental photoconductance is extracted from the low-*
 539 *frequency impedance spectroscopy measurements performed under optical excitation (Figure 8). The dashed line*
 540 *shows the linear variation fit which gives a macroscopic photo-conductance efficiency of $250 \pm 40 \text{ nS.W}^{-1}.\text{cm}^2$.*
 541

542 As mentioned above, $k_0(\lambda)$ in Eq. 6 accounts for the light absorption and for
 543 the inter-particle charge transfer of the photo-generated charge carriers. The fact, that
 544 $k_0(\lambda)$ is maximum at $\lambda = 532 \text{ nm}$ has to do with the transition dipole between initial
 545 and final states involved in the optical absorption process. As a matter of fact, gold has
 546 inter-band transitions between occupied d-orbital and unoccupied s-orbital states
 547 (above the Fermi level) with a maximum absorption around 500 nm wavelength [35].
 548 The inter-band transitions overlap with the plasmonic resonance which is responsible
 549 for the decay of the surface plasmons into hot electron-hole pairs. Therefore, a
 550 maximum efficiency of photo-carrier generation is expected at the plasmonic
 551 resonance as observed in Figure 8. Moreover, hybridization between the metal
 552 nanoparticle and the dodecanethiol electronic states takes place because of the strong
 553 bonding of the thiol molecules with the metal surface. In that case, one may also expect
 554 transitions from the occupied d-orbital states of the gold nanoparticle to the un-
 555 occupied states of the thiol molecule which may also contribute to $k_0(\lambda)$. The
 556 hybridization of the molecule/nanoparticle electronic states still need to be modelled
 557 using quantum mechanics and implemented into DDA-Kirchhoff numerical
 558 simulations in order to fully account for the photo-induced effects in self-assembled
 559 nanoparticle assemblies.
 560

561 5. CONCLUSION

562 To summarize, we presented a theoretical investigation of the plasmoelectronic
 563 properties of self-assembled gold nanoparticle networks in conjunction with
 564 impedance spectroscopy measurements. A photo-electric nano-junction model,
 565 formed by first neighbor nanoparticles, was introduced as an elementary building

566 block of a mesoscopic electrical circuit; the latter was rescaled to allow comparison
567 with experiments performed at the macroscopic scale. Its electric properties
568 (resistance, capacitance, and photo-resistance) were obtained by incorporating electro-
569 dynamic calculations of the local optical properties, based on the DDA method, into
570 Kirchhoff's current-bias equations. An important feature of the theoretical modeling is
571 that the actual spatial sizes and relative positions of the nanoparticles within the self-
572 assembly are taken into account as they determine the local resistance, capacitance and
573 photo-resistance. The charge carrier transport across the nanoparticle network was
574 numerically simulated using the developed DDA-Kirchhoff combined approach, and
575 analyzed in terms of impedance Nyquist's plots and resonance properties. The effect
576 of structural disorder has been addressed because it is critical in understanding the
577 shape of impedance Nyquist plots and resonance curves. The DDA-Kirchhoff
578 numerical simulations were used to determine the percolating conduction paths, their
579 statistical distribution, and the effect of optical excitation. Our main findings are : (i)
580 the plasmonic assisted photo-conductance is responsible for a decrease of the network
581 admittance and impacts both its impedance and susceptance. (ii) the shapes of the
582 impedance Nyquist plot and resonance curve may strongly deviate from, respectively,
583 a semi-circle and a Lorentzian function because of inhomogeneous distribution of
584 relaxation times induced by disorder effects. (iii) the histograms of length and
585 admittance of conduction paths depend on optical excitation intensity. The path
586 impedance and susceptance decrease roughly as the inverse path length. (iv) using
587 quantitative comparison between DDA-Kirchhoff numerical simulations and
588 experimental impedance spectroscopy data, the local photo-conductance of a single
589 nano-junction, with nearly touching nano-particles, is estimated at $18 \pm 4 \text{ nS.W}^{-1}.\text{cm}^2$
590 at the plasmonic resonance. (v) using a close inspection of plasmo-electronic
591 conduction paths, we found that the role of the plasmonic resonance is twofold : first
592 it is responsible for enhancement of the photo-conductance through increased local
593 optical field intensity. Second, the conversion of surface plasmons into photo-
594 generated hot charge carriers allow for inter-particle tunneling over larger distances
595 than thermalized ones.

596 The approach developed in this work is generic and can be used to account for
597 the transduction of light into electrical current in composite materials once the local
598 electric characteristics of the charge transport are implemented in elementary junctions
599 forming an electrical network.

600

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607

608 **CONFLICT OF INTEREST:**

609 The authors declare no conflict of interest.

610

611 **DATA AVAILABILITY:**

612 Data underlying the results presented in this paper are not publicly available at this time but may be
613 obtained from the authors upon reasonable request.

614

615 **SUPPLEMENTARY MATERIAL:**

616 Inter-nanoparticle distance histogram, Normalized measured photoconductance G_{photo} , Schematic of inter-
617 particle energy alignment, Impact of the network dispersion on the depressed semi-circles, Distribution
618 of relaxation times in disordered nanoparticle networks, Impact of the laser irradiation on the depressed
619 semi-circles.
620

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