Electronic Supplementary Information

Towards wireless highly sensitive capacitive strain sensors based on gold nanoparticles

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I. Conception of the capacitive sensor

1.1 Sensor architecture

In granular systems, a simple image can be used to estimate the order of magnitude of the capacitances with a network of conductive nanoparticles (NPs) surrounded with ligands (Figure S1). The overall capacitance $C_{\text{total}}$ can be calculated by:

$$C_{\text{total}} = C_s + C$$  

where $C_s$ is the intrinsic capacitance corresponding to the energy required for an electron to enter a single nanoparticle and $C$ is the geometric capacitance associated to the electro-statistical interactions between a nanoparticle and its neighbors in the NP assembly.

The intrinsic capacitance $C_s$ can be expressed as:

$$C_s = 4\pi\varepsilon_0\varepsilon_r r$$  

where $r$ is the radius of the nanoparticle, $\varepsilon_0$ the permittivity of the vacuum and $\varepsilon_r$ the relative permittivity.

![Figure S1](image)

Figure S1: (a) Schematic of a nanoparticle assembly and the diagram of the electrical relationship between two nanoparticles [1-2].

The geometric capacitance $C$ can be calculated using the $C_{ij}$ capacitance linked to the junction capacitance between two NPs (Figure S1) can be expressed using various models proposed in the literature [3-5]:

On one hand, Leroy and Cordan’s model [6] takes into account the capacitive pair interaction of a NP with the surrounding medium:

$$C_{ij} = 4\pi\varepsilon_0\varepsilon_r r \sinh \left( a \cosh \left( 1 + \frac{l}{d} \right) \right) \times \sum_{n=1}^{\infty} \frac{\sinh \left( 2na\cosh \left( 1 + \frac{l}{d} \right) \right)}{\cosh \left( 1 + \frac{l}{d} \right)}^{-1}$$  

with $l$ the distance between two particles, $r$ and $d$ the radius and diameter of the nanoparticle.
respectively, $n$ the number of nanoparticles in a given volume, $\varepsilon_0$ the permittivity of the vacuum and $\varepsilon_r$ the relative permittivity of ligands.

On the other hand, Quinn et al. [7] has proposed a model based on approximations where the junction capacitance between two NPs can be simplified with the following equation:

$$C_{ij} = \pi \varepsilon_0 \varepsilon_r d \ln(1 + d/l)$$  \hspace{1cm} (4)

A quick calculation of the $C_{ij}$ capacitance gives a capacitance value c.a. the aF. Hence, the assembly of few gold nanoparticles between two single electrodes would lead to a very low capacitance value (i.e. <1 pF) which would be difficult to measure because it could be easily disturbed by surrounding parasitic capacitances. However, capacitive sensors are highly dependent on their dielectric material between electrodes, geometry and shape. Thus, the overall geometric capacitance $C$ could be increased $k$ times using interdigitated electrodes design by multiplying the number of lines of NPs (Figure S2) which integrates these $C_{ij}$ elementary capacitances associated in series and parallel. This $k$ parameter is a function of the surrounding $N$ nearest neighbors of a NP and the geometric features of the interdigitated electrodes such as defined in Figure S1:

$$C = kC_{ij} \text{ where } k = \frac{2Nnp}{L_1 + L_2}$$  \hspace{1cm} (5)

where $C_{ij}$ is the junction capacitance between two NPs, $k$ is the geometrical parameter, $N$ the number of nearest neighbors, $n$ the number of electrode pairs, $p$ the number of nanoparticle layers, $w_1$, $w_2$, $L_1$, $L_2$ the lengths and widths defined in Figure S2.

Hence, the best solution to increase the number of nanoparticles bonded in parallel is to have a long and thin line of nanoparticles surrounded by interdigitated electrodes. Then based on Eq. 5, it is possible to calculate the total capacitance values for geometry with given dimensions.

Figure S2: (a) Schematic view of the capacitive strain sensor configuration with interdigitated electrodes (b) geometric electrode parameters and distribution of the nanoparticles between the electrodes

### 1.2 Sensor strain sensitivity

By using the total capacitance at rest (Eq. 4 and Eq. 5) $C_0 = k \pi \varepsilon_0 \varepsilon_r d \ln(1 + d/l)$ and the total capacitance under uniaxial strain: $C = k \pi \varepsilon_0 \varepsilon_r d \ln(1 + d/(l + \Delta l))$ where $\Delta l = \varepsilon(l + d)$, one could obtain the uniaxial variation of the capacitance as a function of the strain, the diameter of NPs and the inter-nanoparticle distance:

$$\Delta C = C - C_0 = k \pi \varepsilon_0 \varepsilon_r d \ln(1 + d/(l + \varepsilon(l + d))) - \ln(1 + d/l))$$
\[ \Delta C = k \times \pi \varepsilon_0 \varepsilon_r d \times \ln \left( \frac{1 + d(l + \varepsilon(l + d)))}{1 + dl} \right) = k \times \pi \varepsilon_0 \varepsilon_r d \times \ln \left( \frac{l(1 + \varepsilon)}{l(1 + \varepsilon) + \varepsilon d} \right) \]

\[ \Delta C = k \times \pi \varepsilon_0 \varepsilon_r d \times \ln \left( \frac{l(1 + \varepsilon) + \varepsilon d}{l(1 + \varepsilon) + \varepsilon d} \right) = k \times \pi \varepsilon_0 \varepsilon_r d \times \ln \left( \frac{l - \varepsilon d}{l + \Delta l} \right) \]

\[ \Delta C \approx -k \times \pi \varepsilon_0 \varepsilon_r d \times \frac{\varepsilon d}{l + \Delta l} = -k \times \pi \varepsilon_0 \varepsilon_r d \times \frac{d^2}{(l + \Delta l)} \times \varepsilon \]

\[ \frac{\Delta C}{C_0} \approx \frac{C - C_0}{C_0} \approx -k \times \pi \varepsilon_0 \varepsilon_r d \times \ln \left( \frac{1 + d}{l} \right) \times \varepsilon \approx -\frac{d}{l \ln (1 + \frac{d}{l})} \times \varepsilon \]

At the end, the total relative capacitance variation is:

\[ \frac{\Delta C}{C} \approx -\frac{d}{l \ln (1 + \frac{d}{l})} \times \varepsilon \]  \hspace{1cm} (6)

where \( \varepsilon = \frac{\Delta l}{l} \) is the strain applied to the sensor.

The result of these calculations enabled us to design the adequate NP assembly form and dimensions. The dimensions presented in Table 1 were chosen to obtain an initial capacitance of nanoparticles around 1 pF, measurable with available instruments and overcoming parasitic capacitances. The theoretical capacitance values are presented for three different nanoparticle diameters using the two models studied above. It is worth noting that the chosen dimensions are also based on compensation between the optimum values obtained by simulation and the limitation of the fabrication process (e.g. laser lithography resolution…).

Table S1: Capacitance calculation of three NP-based sensors with a surface area of 1 mm² and different sizes of gold nanoparticles integrated between interdigitated electrodes (width = 5 μm and interdigitated distance = 5 μm).

<table>
<thead>
<tr>
<th>NP diameter</th>
<th>( C_S )</th>
<th>( C_{ij} ) and ( C ) using CORDAN/LEROY’s model [6]</th>
<th>( C_{ij} ) and ( C ) using QUINN’s model [7]</th>
<th>Experimental capacitances</th>
<th>Sensor dimensions</th>
</tr>
</thead>
</table>
| 7 nm        | 0.8 aF   | \( C_{ij}=0.5 \) aF  
\( C=0.43 \) pF | \( C_{ij}=0.8 \) aF  
\( C=0.68 \) pF | \( C_{exp}=1.09 \) pF  | ![Image](image.png)  |
| 12 nm       | 1.5 aF   | \( C_{ij}=1.1 \) aF  
\( C=0.90 \) pF | \( C_{ij}=1.8 \) aF  
\( C=1.46 \) pF | \( C_{exp}=1.6 \) pF  |
| 14 nm       | 1.7 aF   | \( C_{ij}=1.3 \) aF  
\( C=1.10 \) pF | \( C_{ij}=2.2 \) aF  
\( C=1.80 \) pF | \( C_{exp}=1.465 \) pF |

For the same three different nanoparticle diameters, the experimental capacitance values are presented for comparison with theoretical ones. It is worth noting that the experimental values are founded in the range of the theoretical ones despite some small variations due to the difficulty to form a perfect NP assembly over such a large area of 1 mm² interdigitated electrodes.
II. Chemical synthesis of gold nanoparticles

HAuCl₄·nH₂O (purity: 99.99%) was purchased from Alfa Aesar. Triphenylphosphine (PPh₃) (98%) was purchased from Strem Chemicals. Dodecanethiol (98%), toluene (99.7%) and tertbutylamine–borane complex (97%) were purchased from Sigma Aldrich. All chemicals were used as received without further purifications.

7, 12 and 14nm gold nanoparticles were synthesized using two routes.

The 7 nm gold nanoparticles were synthesized following the protocol described by Zheng et al. [8]. A gold precursor (AuPPh₃Cl) soluble in organic solvents was synthesized by reacting, under stirring, 304 mg of commercial HAuCl₄·nH₂O with 590 mg of PPh₃ in 9 mL of ethanol for 15 min [9]. After washing with 30 mL of ethanol and drying under vacuum, a white powder was recovered (yield ≈ 40%). In a three-neck glass flask, 0.125 mmol of AuPPh₃Cl and 62.5 μL of dodecanethiol were dissolved in 10 mL of toluene and degassed under argon. After 30 min, 1.25 mmol of the tert-butylamine–borane complex was added quickly in 10 mL of toluene. Under vigorous stirring, the mixture was heated at 100 °C for 1 hour leading to the formation of 7.1 ± 0.5 nm Au nanoparticles. Then, the mixture was cooled down to room temperature and the NPs were washed by addition of 30 mL of ethanol, centrifuged at 3900 rpm for 5 min and redispersed in 4 mL of toluene. This procedure was repeated one more time and resulted in a colloidal suspension of spherical Au NPs in toluene at a concentration of about 2 × 10¹⁵ NPs per mL as presented in the Figure S3.

The 12 and 14 nm gold nanoparticles were synthesized following the protocol described by and al. [10]. They were obtained by quickly injecting a solution of 50 mg (0.15 mmol) of tetrachloroauric acid in 1.0 g (3.7 mmol, 1.2 ml) of oleylamine and 1.0 ml of toluene into a boiling solution of 1.7 g (6.4 mmol, 2.9 ml) of oleylamine in 49 ml of toluene. Over the course of 5-10 min, the color of the reaction mixture changed to bright yellow and then gradually to deep red. Heating was stopped after 2 hours, and then, the mixture was cooled down to room temperature. ~15 nm Au nanoparticles were obtained analogously by using 20 mg (0.06 mmol) of the gold precursor. Oleylamine ligands were then exchanged with C12-SH following our own recipe: In a clean 100ml round-bottom flask, 22ml of as-synthesized gold NPs solution were added. Under stirring, a toluene solution containing thiols ligands were added dropwise following by stirring at ambient for 1 hour. The amount of thiols was calculated to be precisely equal to 2 times the quantity mandatory to totally cover the available gold NPs surfaces (2 equivalents). Solution of gold NPs remained stable and red after 1 hour at ambient. Then, the nanoparticles were washed by addition of 18 ml of ethanol, centrifugation at 9000 rpm during 5 minutes and redispersed in 1 ml of toluene. This procedure was repeated one more time and lead to a colloidal dispersion of spherical gold nanoparticles in toluene at a concentration of about 2.10¹⁵ NPs/ml as presented in the Figure S3.

![7 nm](image1.png)  ![12 nm](image2.png)  ![14 nm](image3.png)
Figure S3: Transmission electron microscopy (TEM) images and corresponding size distributions of three types of gold NPs protected by dodecanethiol (C12) ligands.

III. Capacitive Strain Gauge Fabrication (lift-off method):

A 125 µm polyimide film (Upilex) substrate was chosen due to its high thermal resistance and its dimensional stability after strain. After cleaning with acetone and deionized water, gold electrodes were structured on the surface of this substrate using the lift-off method. First, a sacrificial layer was spin-coated using the S1805 positive photosensitive resist. This step was followed by a soft bake for 1 min at 115 °C to obtain a uniform layer of some hundreds nanometers. A reverse pattern was then created in the sacrificial stencil layer by laser photolithography (Dilase 650). This was done by etching openings through the layer by a laser beam of a 325 nm wavelength and a diameter of 1 µm. External parts of the electrodes that serve further for electrical contacts were etched by a laser beam of 10 µm to speed up the process since the resolution is not important in this zone. To remove the residue in the holes, the sample was rinsed in the resist developer (AZ726MF) with 1 min of stirring, development was stopped by water. Then, a 50 nm gold Au layer was deposited over the entire surface of the substrate by IBS-E ion beam sputtering. When the sacrificial layer was removed by washing (in acetone for about one hour), the gold on top was lifted and washed together with the sacrificial layer below. After taking-off, the Au target material only remained in areas where it had direct contact with the substrate.

IV. Temperature-dependent electron transport

An estimation of the capacitance values of the sensors can be obtained by the electron transport analysis method which is based on the extraction of the charging energy $E_C$ via the resistance data as a function of temperature. Indeed, the total resistance $R$ encountered by the electrical current flowing from one electrode to another, can be expressed as [1]:

$$R = \frac{L}{NWL} \cdot a \cdot R_{12} \cdot e^{\beta l} \left( \frac{1 - e^{E_C/k_B T}}{1 - (1 - E_C/k_B T) \cdot e^{E_C/k_B T}} \right)^2$$

where $L$, $W$ and $H$ are the geometrical dimensions of the NP assembly: length, width, height, $(e^{-\beta l})$ is the term depending on the gap $l$ between adjacent nanocrystals and the tunneling decay constant $\beta$ of electrons along the ligand molecules represents the electron tunneling, $a$ is the lattice spacing of the NP assembly. By considering a regular cubic lattice for the sake of simplicity, $a$ can be written as $(d + l)$ where $d$ is the NP diameter and $l$ the distance between adjacent nanocrystals. $R_{12}$ is the temperature-independent resistance term:

$$R_{12} = \frac{\hbar}{8\pi e^2} \cdot \left( A^2(E_F) \cdot \rho^2(E_F) \right)^{-1}$$

depending on $\hbar$, the reduced Planck constant, $e$ the elementary charge, the electron density of states at the Fermi level $\rho$ and the exponential pre-factor $A^2(E_F)$, deduced from the coefficient of transmission $|T(E_F)|^2 \sim e^{-\beta l}$ at the Fermi level of a nanoparticle [11-12]. The last term (between parentheses) depends on $T$ the absolute temperature, $k_B$ the Boltzmann constant, $E_C$ the Coulomb charging energy that arises from the
Coulomb interactions of electrons in occupied single electron states of one nanoparticle with unoccupied states of the neighboring one.

The experimental results can be compared to the capacitance values obtained by the models presented previously. The resistance at rest of the 7nm NP-based sensor extracted from the linear fitting of the $I-V$ curves is $R_0 = 0.617 \ \text{M}\Omega$ at room temperature. The electron transport properties investigated as a function of temperature (Figure S 4). The resistance at rest $R_0$ shows an exponential increase as the temperature decreases. This trend was previously reported for different NP films as a consequence of the presence of NP coating ligands that act as tunnel barriers between conductive NPs.[1, 13-14] The contribution of $E_c$ in the resistance of a capacitance coupled system of NPs was determined by the exponential fitting of $R(T)$ using the previous equation. An average value $E_c = 25 \pm 2 \ \text{meV}$ was deduced from the exponential fitting of $R(T)$ data.

\[
E_c = \frac{e^2}{2C}
\]  

(8)

A capacitance value of 0.78 pF was deduced from this $E_c$ value when considering an average Au NP diameter $d = 2r = 7 \ \text{nm}$, an inter-particle distance $l = 1.2 \ \text{nm}$ for ligands dodecanothiol C$_{12}$, $\varepsilon_r = 2.3$ typical for dodecanethiol C$_{12}$ self-assembled and $N = 12$ for a 3D layers hexagonal array. This capacitance value was found in very good agreement with values determined by the previous calculation and further by the experimental measurements.

![Experimental data vs. fitting curve](image)

*Figure S4: Electrical resistance at rest $R_0$ of a capacitive 7 nm NPs based strain sensor as a function of temperature.*

V. Inter-particle distance measurement method

The electron transport properties of NP assemblies are governed by the inter-nanoparticle distances. In order to estimate the error bar of the relative capacitance variation of our capacitive strain sensors, this inter-nanoparticle distance was calculated by an auto-correlation processing performed with Gwyddion software (http://gwyddion.net/) using SEM images containing a high number of NPs (Figure S5a). The interference fringes of the SEM image presented in Figure S5b shows a uniform distribution of the nanoparticles throughout the surface. From the profile of the interference fringes (Figure S5c), we deduced the inter-NP distance can vary in between 1.2 nm +/-0.4nm.
Figure S 5: (a) Typical Scanning Electron Microscopy (SEM) image of a the active area of a capacitive 14 nm-based strain sensor (b) Interference fringes of the SEM image after processing by the "Gwyddion" software, showing an uniform distribution of the nanoparticles throughout the surface, (c) profile of the image presented in (b) from which the distance between two particles can be deduced.

References