Heat and electron flow under plasmonic excitation in nanoparticle assemblies: application to innovative capacitive strain gauges

Acronym: **PLASMOTRONIC**

I. Project's presentation:

I.1 Abstract:

The PLASMOTRONIC project is devoted to the study of light to current conversion in metal nanoparticle assemblies coated with ligand molecules. The light absorption by surface plasmons and their decay into electron-hole pairs and then into phonons is a complex process at the origin of photo-current and photo-thermal generation. Electrically connected nanoparticle membranes, either free-standing, or deposited on flexible substrates, open access to intrinsic plasmo-electronic properties. The carrier charge generation and transport mechanisms are still unclear and require further experimental and theoretical investigations before reaching a full understanding of the physics of these nano-materials and turning them into functional devices. The PhD work is devoted to the caracterisation and understading of the plasmoelectronic properties of such nanoparticle assemblies which are very interesting for their use **as capacitive strain** sensors implemented into aeronautics, space or embedded systems. The PhD student will participate in making a major contribution in wireless ultra sensitive sensors. The project involves research teams from LPCNO and CEMES labs in Toulouse sharing complementary skills and experimental as well as computational facilities.

I.2 State of the art and motivations

Assemblies of conductive colloidal nanoparticles protected by organic ligands have attracted considerable attention during the last decade because of their unique collective properties arising their inter-particle electronic, optic or magnetic coupling effects which render them potentially appealing for several sensing applications (gas sensors, temperature sensors, strain gauges…). Moreover, plasmonic metal nanostructures have attracted extensive research and have been exploited for enhancing the performance of various optoelectronic devices [-].

While nanoparticle systems made possible the development of highly sensitive, robust, and low consumption sensors, their industrial exploitation for embedded systems is still in its infancy. To advance industrial applications based on nanotechnology for aeronautic and spatial applications, nanotechnology must then bring new features and/or a tenfold increase in device performance while reducing production and operation costs.

Therefore, the coupling between heat, charge transport and surface plasmons in metal nanostructures has emerged as a strong driving force of the "plasmo-electronics" field which could provide a new class of light responsive nanomaterials based devices [-]. It had been discovered that plasmonic excitations can influence macroscopic flows of charges and, conversely, that charging of metal nanoparticles (NPs) can impact their plasmonic response. In particular, both positive and negative photoconductivity, i.e. either conductivity increase or decrease on irradiation with light tuned to the particles' surface plasmon resonance, have been evidenced on a new class of nanoparticle-based materials [].

At the same time, recent advances in self-assembly of NPs have allowed to obtain conductive, ultra-thin, freestanding close-packed NP arrays, so called NP membranes (NPMs) [-].

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Very recently, at LPCNO, we have achieved a robust process for the fabrication and electrical connection of monolayer thick freestanding NPMs (Figure 1) [-]. We were able to investigate intrinsic plasmo-electronic properties of monolayered hexagonally close-packed NP arrays **with no impact of the elaboration process and no influence of the substrate.** We showed that the coupling between plasmonic excitation and electron transport in such devices exhibits a non-linear increase of the photo-conductance with laser intensity (Figure 2b). This phenomenon was interpreted as due to both temperature dependence of the electrical conductance and to charge carrier trapping/detrapping dynamics. **However, efforts must be undertaken for unraveling the complex underlying physics of the coupling between plasmonic and both electron and heat transport in such complex hybrid systems.**

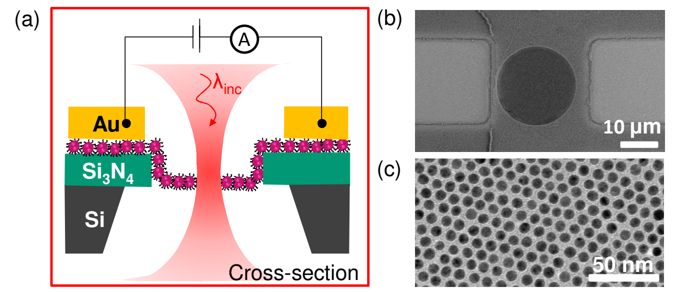

Fig 1: a) Schematic cross-section of a contacted freestanding monolayered Au nanoparticle (NP) membrane (NPM), under laser beam illumination. b) Scanning electron microscopy image of a freestanding monolayered dodecanethiol coated 7 nm Au NP membrane suspended over a 20 µm wide Si_3N_4 stencil aperture substrate with two gold microelectrodes as contacts. c) transmission electron microscopy (TEM) image of a freestanding monolayered membrane of 7 nm dodecanethiol coated Au NPs.

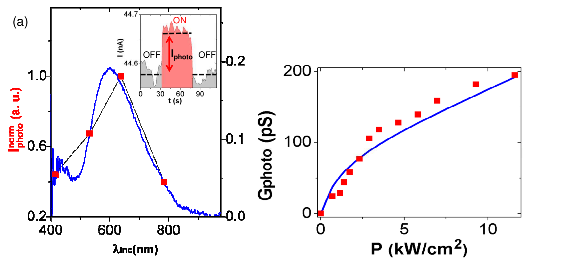

Fig 2: a) Normalized plasmonic photocurrent and optical extinction spectrum of a freestanding monolayered NPM as a function of incident wavelength λ_{inc}. Inset: Electrical current as a function of time with on/off laser beam (λ_{inc} = 638 nm, I_{Laser} = 5.2 kW/cm^2, +1V). The OFF and ON states are highlighted by grey and red areas, respectively. b) Plasmon-induced conductance G_{photo} (red squares) as a function of illumination I_{Laser}.

Indeed, the conversion of light into current, in self-assembled metal nanoparticle systems, occurs through the excitation of surface plasmons and their decay into electron-hole pairs and phonons. Energy relaxation through emission of phonons leads to heat generation and hence to the hyperthermia phenomena. Moreover, the mechanisms of charge transport through the composite medium formed by the metal nanoparticles and their surrounding ligands molecules are multiple and still unclear: quantum tunneling, variable range hopping, phonon assisted, excitation transfer assisted, carrier trapping/detrapping...

An ambitious objective of the PhD work is to bring together the very active research areas of <u>plasmonic, heat and electron transport</u> both for studying the underlying fundamental physics and for developing applications oriented new functional materials. While colloids composed of metallic nanoparticles (NPs) stabilized by organic ligands have been used to fabricate hybrid nanoparticles/molecules networks contacted by nanoelectrodes [-], the **fabrication of model systems allows** to investigate the influence of the nanoparticle characteristics (size, shape and metal), the ligand charge, the inter-nanoparticle distance, the electrostatic environment, the substrate…

I.3 Realization plan:

<u>**METHODOLOGY:**</u>

Our methodology is based on a feedback loop involving fabrication processes, various characterization techniques and numerical simulations:

1 - WP1 (LPCNO): Fabrication of <u>nanoparticles and samples</u> using the facilities available at the NANOTECH platform of LPCNO (chemist lab, laser and stencil lithography, optical masker, organization of gold colloids by CSA...).

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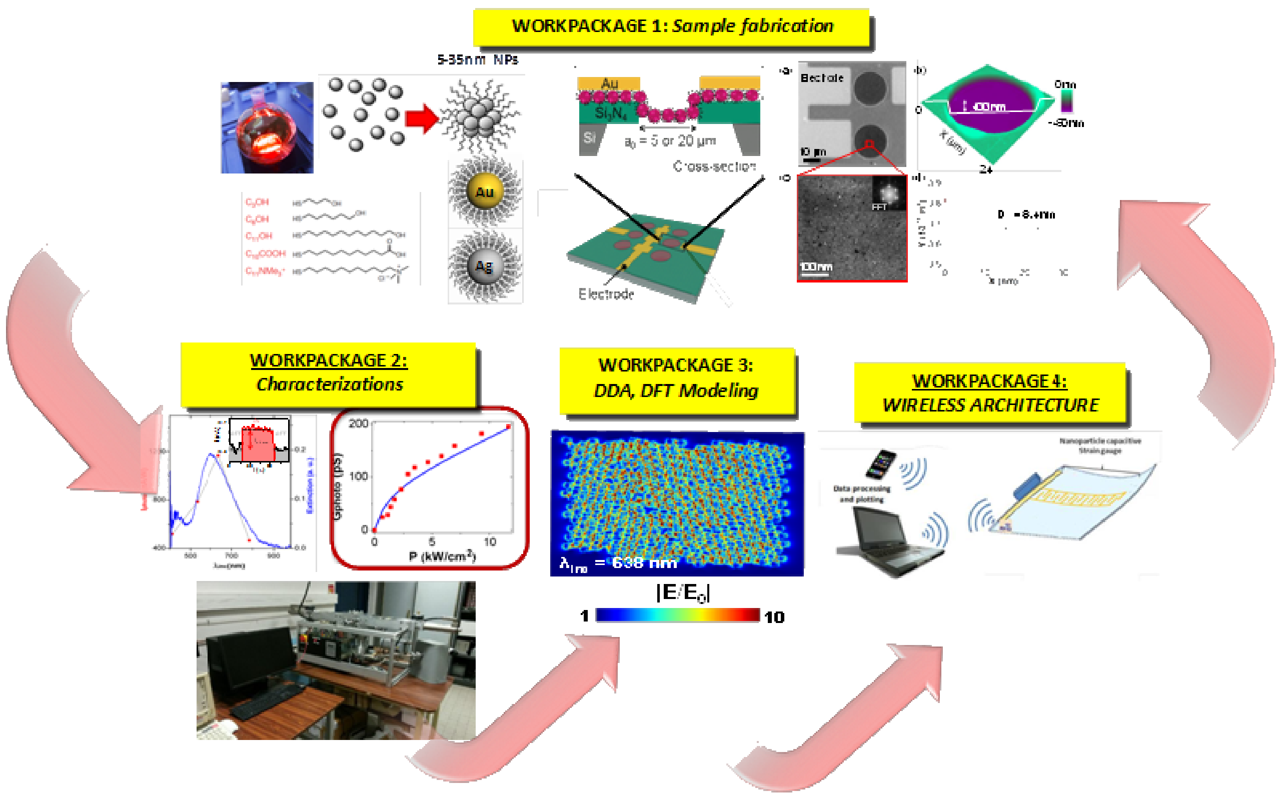
2 - WP2 (CEMES+LPCNO): optical, electrical and thermal characterizations with strain applied in situ thanks to a home-made micromachine vacuum chamber operating both at low and high temperatures and under laser illumination.

3 - WP3 (CEMES): simulations based on numerical calculations will be achieved using the discrete dipole approximation method DDA to compute the plasmonic response of NPs assemblies, as well as the temperature distribution induced by a plasmonic photo-thermal process. Numerical simulations will aslo be used to optimize the design of NPs (shape, size, inter-NP distance) with ligands (insulating or non-insulating) and to support the interpretations~~,~~

4 – WP4: (LPCNO): wireless design of the electrical read-out



PLASMOTRONIC is a nanotechnology project in which simulations guide the design of nanostructures and the interpretation of the experimental results.

In a first step, we will synthesize and optimize the design of metal NPs ((Au, Ag), shape, size, distances, ligands) to optimize both their plasmonic and electrical responses. **Then, we will focus on the fabrication of <u>two types of model samples</u> based on self-assembled metal nanoparticles:**

- Stencil-processed samples dedicated to the formation of free-standing monolayer NPMs,
- Flexible polyethylene terephthalate (PET) samples for monitoring the plasmonic and electronic transport properties-in the sub-10 nm inter-particle gap regime.

1 - Stencil-processed samples:

The **stencil lithography technique,** developed at LPCNO, is based on the self-assembly of NPMs at the liquid / liquid interface [-]. NPMs suspended above apertures (Fig.1a), e.g. free-standing monolayers of Au NPs array with hexagonal close-packed long range order (Fig. 1c), can be obtained using this technique. In addition, this **method prevents any degradation and contamination from conventional lithography and gives access to intrinsic NPs properties (no influence of the substrate)**. Electrical connections of the individual membranes will be achieved by gold deposition through a custom-made stencil (Fig.1b). The transduction of the plasmonic excitation into electrical current of this membrane is presented in Fig2a. The amplitude of the plasmon-induced photo-current strongly depends on the excitation wavelength, illumination power, applied voltage and temperature. In these samples we will combine electron transport measurements, optical excitation and Stokes/anti-Stokes Raman scattering measurements of the local temperature in order to connect the plasmonic pumping of the photo-current and the thermal induced transport.

2 - Studies with Flexible PET samples:

NPMs will then be coated on flexible substrates using the Convective Self Assembly technique (CSA) [-]. The samples will submitted to strain in a home-made micro-machine which allows monitoring the inter-particle distance in the sub-10nm length scale. This will give access i) to the control of the plasmonic response, which is determined by the electro-magnetic near-field coupling between the nanoparticles ii) to the monitoring of the electron tunneling transport regime. The measurements will be carried out from low (10K) to high (450K) temperatures to access the thermal properties of the nanoparticle assembly in connection with electron transport.

Also, the optically induced heating of the NPMs is expected to depend on the nanoparticle separation due to shift of the plasmonic response and to heat diffusion. Spatially resolved photo-current measurements combined with Stokes/anti-Stokes Raman measurements will be used to probe the plasmonic, electronic and thermal properties of the NPMs under applied strain. Mapping of the photocurrent and of the Raman signal will give access to the spatial distribution of the plasmoelectronic efficiency. Moreover, the characteristic time constants (rise and decay of photocurrent) will be investigated as a function of the NPs characteristics including their inter-particles distance.

Interpretations of the experiments will be based on modeling of the heat generation, diffusion and dissipation in the nanoparticle assembly which is required for fully understanding and controlling the plasmonic and the thermal properties of these complex hybrid media.

I.4 Novelty of the project proposal: beyond the state of the art.

One main challenge addressed in the PLASMOTRONIC project is to turn the fundamental knowledge acquired on the optical, electronic and heat properties NPMs into innovative applications.

- From the fundamental point of view: The plasmonic enhancement of the optical absorption of NPMs would lead to efficient light conversion. This plasmonic-based light harvesting strategy will be combined with photoluminescence quenching for increased electron-hole pair lifetime and minimal current loss. This is challenging and requires accurate shaping of the plasmonic density of states based on advanced modeling approaches.

- From the application point of view: The monitoring of the photo-current via plasmonic resonances would constitute a major advance for technological applications in opto-electronics especially for the design of a new generation of strain sensors based on:

i) the monitoring of the NPMs plasmonic resonance by an applied DC voltage,

ii) the high sensitivity of the plasmonic induced photo-current to the optical excitation (incident power, wavelength)

iii) its control using an applied strain in the case of NPMs coated on flexible substrates.

In particular, as the PET substrate is transparent in the visible range, the sensors will exploit the spectral shift of the plasmon resonance due to the coupling between NPs. Thanks to the unprecedented characteristics of the nanoparticle properties based devices (low consumption, low cost) coupled with a wireless solution, those nano-material based sensors could be deployed at large scale in order to monitor extensive systems in aeronautics, space and embedded systems. This features is crucial since the sensor market is growing very rapidly ($91.5 billion in 2016 with annual growth of 7.8% [13]), driven in particular by the need for companies to develop new functionalities exploiting the latest developments in nanotechnology. In terms of research valuation, the LPCNO Nanotech group has a great experience with its spin-off company NANOLIKE (http://www.nanolike.com/) and patents on touch sensitive screens now exploited by NANOMADE[14] company. The plasmo-electronics project may therefore lead to novel sensing applications which can be developed and commercialized in partnership with these companies.

II. Teams presentation:

PhD directors :

LPCNO	CEMES
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Coherence of the proposal

This collaborative research involves two complementary labs from Toulouse University-CNRS: LPCNO (Laboratoire de Physique et Chimie des Nano-Objets)**,** and CEMES (Centre d'Elaboration de Matériaux et d'Etudes Structurales). This doctoral work requires a **MULTIDISCIPLINARY** work at the interface between CHEMISTRY and PHYSICS. The LPCNO and the CEMES are laboratories where physicists and chemists work together.

*** Project coordinator.** Pr. Jeremie Grisolia (LPCNO) has been involved in more than 18 research projects. He co-authored more than 80 research papers, h-index 15, RG Score ~34 (> 95% RG members). For more than 15 years, my research interests have been focusing on the study of the transport properties of nano-objects (silicon nano-particles embedded in SiO_2, assemblies of metal nanoparticles (Or, Ag, ...) for the realization of gas sensors and strain gauges), and the development of nanotechnology processes ("ultimate" MOS transistors, stencil lithography, dielectrophoresis, nano-imprint, electronic lithography ...)

* **The LPCNO - Nanotech group** involves a multidisciplinary team: PHYSICISTS and CHEMISTS. Chemists focus on innovative nanoparticles synthesis. Physicists develop innovative techniques for directed assembly of colloidal nano-objects from their liquid phase onto specific areas of rigid or flexible substrates. In particular, they have been developing during 10 years an innovative method called stencil lithography in collaboration with EPFL Lausanne and they are specialized in convective self-assembly (CSA) of colloidal nanoparticles, an efficient way to form compact arrays of nanoparticles on large areas (several cm^2) from a drop of a colloid suspension dragged onto a substrate [-]. They have also a strong experience in electronic transport measurements based on sample with assemblies of metallic and semiconductor nano-objects. Hence, in particular since 2009, our team proposed a novel nanoparticle based strain gauge to monitor local deformation with a high sensitivity. Figure 1 shows a typical active area of this gauge that consists of parallel wires, a few micrometers wide made of colloidal gold nanoparticles. These nanoparticles are typically 14nm in diameter and are surrounded by organic ligands which form a thin dielectric barrier. The wires of nanoparticles, deposited on a flexible polymer substrate are connected by gold electrodes. This resistive nanoparticle sensor operation is based on the variation of electrical conduction in the assembly of metallic nanoparticles subjected to mechanical strain. As a first approximation, the current passes between the nanoparticles by electron tunneling through a barrier imposed by ligands. The overall resistance of the sensor varies thus exponentially with the strain (Figure 1c).

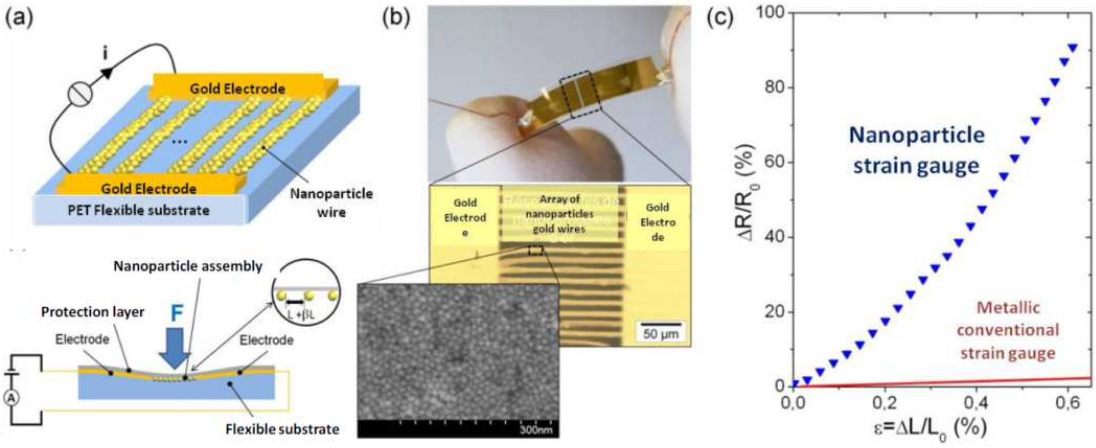

Figure 1: (a) Schematic diagram of a resistive nanoparticle strain gauge, (b) photograph of a strain gauge made of 14 nm gold nanoparticles (top) - image by optical microscopy the active area of the gauge (middle) and image by scanning electron microscopy of the arrangement of nanoparticles (bottom). (c) Relative change of resistance of the strain gauge shown in (b) as a function of strain (the red curve represents the typical response of a conventional metal gauge)

The extreme sensitivity of these nanoparticle-based strain gauges (compared to conventional metal gauges (Figure 1c)) has been demonstrated with obtaining reproducible changes in resistance of about 90% to 0.6% strain. Strains of several % have been measured with this type of sensor. Part of those results has been obtained by INSAT/LPCNO during the project NanoComm funded by the Nano-Innov/RT program of the ANR (2009-2011) – France whose goal was to develop a new generation of sensor networks in view of industrialization for aeronautical applications. The partners of this project were LAAS, CEA-LETI, CIRIMAT, EADS Innovation Works, Nanomade Concept, IMS. The Nanocomm project success allowed us in 2014 to engage further in projects dedicated to the introduction of disruptive innovations in aerospace industry via an ESA Innovation Triangle Initiative (ITI) project and a DGA project. This latter project involves industrial companies (e.g. Intespace, …) or start-up coming from our team to industrialize sensors (e.g. Nanolike…) for the realization of resistive nanoparticle strain gauges in aerospace industry. **The project goal was to bring their performance in a representative environment (temperature, variable humidity, electromagnetic radiation...) and the technology from TRL3 to TRL5.**

Researcher's implications: physicists: J. Grisolia (Pr), L. Ressier (Pr) and Benoit Viallet (MCF), chemist: Louis Vaure (Post-doc), will be in charge of the sample elaboration, electron transport characterization as a function of temperature and applied strain.

* **The CEMES** researchers involved in the project are members of the Nano-Optics and Nanomaterials for Optics. Research activities aim at developing new optical instruments and new materials which can be implemented in novel opto-electronic devices. Electron microscopy and optical spectroscopy facilities are available at CEMES, In particular 4 complementary Raman, photoluminescence, dark-field imaging and micro-reflectance systems will be used in the PLASMOTRONIC project. Advanced modeling of the optical properties of semiconductor and metallic nano-materials and nano-structures is a strong know-how of involved CEMES researchers. In particular, numerical simulations based on commercial and home-developed softwares will be used to model the plasmonic properties of NPMs.

Researcher's implications: A. Mlayah (full professor) is in charge of the optical micro-spectroscopy studies including Raman, micro-reflectance and local I(V) light-to-current investigations. Simulations of the plasmonic properties based on the discrete dipole approximation will be performed on the CALMIP HPC facilities.

- 5 REFERENCES FROM PROJECT RESEARCHERS:

Ref 1: R. Marty, et al. Plasphonics : local hybridization of plasmons and phonons. Optics Express, 21, 4551 (2013)
Farcau C,et al. Journal of Physical Chemistry C, 115(30), pp. 14494-14499 (2011).

Ref 2: J. Grisolia et al,. Nanotechnology 26 (33) : 335702 August 2015
Ref 3: M. Gauvin et al. *Nanoscale*, ***2016,*** *8*, ***16162 – 16167***
Ref 4: « Surface tactile et procédé de fabrication d'une telle surface ». L. RESSIER, B. VIALLET, J. GRISOLIA /LPCNO (INSA-CNRS) et L. Songeon, E. Mouchel et L. Czornomaz(Nanomade). Co-propriété avec le CNRS et l'INSA. Brevet n°10/56387
Ref 5 : Towards wireless highly sensitive capacitive strain sensors based on gold colloidal nanoparticles. H. Nesser, J. Grisolia†, T. Alnasser, B. Viallet and L. Ressier. Nanoscale, 2018, DOI: 10.1039/C7NR09685B.

III. Perspectives for the PhD student:

3.3 Professional perspectives for the PhD:

The results obtained in the frame of the PLASMOTRONIC project will be submitted to high impact factor scientific journals, as the addressed research topics are highly competitive and are of strong interest for the large "electron transport", "plasmonics" and "thermal processes" communities. Rapid communication of the results to the scientific community will occur in the frame of international conferences. Since the PLASMOTRONIC project is based on the design of novel nano-material architectures, new hybrid plasmonic-excitonic opto-electronic devices are expected to come out. The student will then of course be prepared for the academic professions: researcher, lecturer, research engineer but also to the R & D professions thanks to this project turned to the applications and to our industrial partners.

3.4 Training, integration and international mobility actions for the doctoral student:

PLASMOTRONIC project contributes to the development of nano-science and technology which have strong societal impact and are therefore the subject of interest for the general public. The PhD will then be involved in several scientific diffusion operations, through:

- participation to several programs of scientific diffusion for scholars ("Science et citoyens", "Nanoschool – CNRS at Lycée Saint Sernin, "Atelier Objectif Science" "Fête de la science", action "high school teachers in your labs"…), journée "profs dans les labos".
- participation to GDRs (Molecular Plasmonics) and organisation of a new GDR (Nanocrystals embedded in Dielectrics for Electronics and Optics),
- participation to the organization of national ("GDR NACRES,) and international conferences.

3 – Our project has links with our academic partners such as: MEMS group from EPFL Lausanne: https://people.epfl.ch/juergen.brugger?lang=fr in the name Juergen Brugger, RISE University in the name of …

IV. <u>References related to the project</u>

REFERENCES

1 - K. R. Catchpole et al. Appl. Phys. Lett., 2008, 93, 191113.
2- H. A. Atwater et al. Nat. Mater., 2010, 9, 205–213.
3 J. Liao et al. Chem Soc Rev, 2015, 44, 999–1014.
4- T. Hashimoto et al. Appl. Phys. Lett., 2013, 102, 083702.
5- P. Banerjee et al. ACS Nano, 2010, 4, 1019–1025.
6- H. Nakanishi et al. Nature, 2009, 460, 371–375.
7- M. A. Mangold et al. Appl. Phys. Lett., 2009, 94, 161104.
8- M. A. Mangold et al. J. Am. Chem. Soc., 2011, 133, 12185–12191.
9- K. E. Mueggenburg et al Nat Mater, 2007, 6, 656–660.
10- J. He et al. Small, 2010, 6, 1449–1456.
11- J. Liao et al. Small, 2011, 7, 583–587.
12- M. A. Mangold et al. ACS Nano, 2012, 6, 4181–4189.
13–C.Dumas et al. Phys. Stat. Solidi A 204, No. 2, 487–491 (2007) / DOI 10.1002.
14- R. Diaz et al., Nuclear Instruments and Methods in Physics Research B 272 (2012) 53–56. NIMB,

REFERENCES FROM PROJECT RESEARCHERS:

16 - R. Marty, et al. Plasphonics : local hybridization of plasmons and phonons. Optics Express, 21, 4551 (2013)
17 - Arbouet et al.. New Journal of Physics (2014)
18 - Cosmin Farcau et al. ACS Nano, 2010, 4 (12), pp 7275–7282 (2010)
19 -Farcau C,et al. Journal of Physical Chemistry C, 115(30), pp. 14494-14499 (2011).
20 -. J. Grisolia et al,. Nanotechnology 26 (33) : 335702 August 2015
21 - Lucas Digianantonio et al.. Journal of Physical Chemistry C - 10.1021/acs.jpcc.6b00822 (2016)
22 - M. Gauvin et al.. Nanoscale 2016 8 (22), 11363-11370
23 - M. Gauvin et al. Nanoscale, 2016, 8, 16162 – 16167
24 - « Surface tactile et procédé de fabrication d'une telle surface ». L. RESSIER, B. VIALLET, J. GRISOLIA /LPCNO (INSA-CNRS) et L. Songeon, E. Mouchel et L. Czornomaz(Nanomade). Co-propriété avec le CNRS et l'INSA. Brevet n°10/56387

25 Towards wireless highly sensitive capacitive strain sensors based on gold colloidal nanoparticles. H. Nesser, J. Grisolia†, T. Alnasser, B. Viallet and L. Ressier. Nanoscale, 2018, DOI: 10.1039/C7NR09685B.