# Numerical Simulations for Designing Wireless Electrochemiluminescence Imaging Microdevices

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## 1. Introduction

### BiPolar Electrochemistry (BPE)

BPE is an elegant electrochemical wireless technique based on the use of a conducting object (i.e. a mono-electrode) which, if immersed in a sufficiently high electric field, is polarized into two poles, one of which acts as the anode and the other as the cathode simultaneously [1].

The usual pre-dimensioning techniques for the BPE show that ECL implementation in microsystems was not feasible due to the high values of the required applied voltage [1]-[2]-[3]-[4]. However, thanks to numerical dimensioning, we could perform BPE in a geometric planar silicon restriction (micropore of size 20 µm x 10 µm) which is easy to fabricate as substrates are silicon, silicon oxide and PDMS [3]-[4].

### ElectroChemiLuminescence (ECL)

ECL is a phenomenon of light emission resulting from an initial electrochemical reaction [2]. Today, ECL is used for detecting biomolecules (DNA, RNA, biomarkers). Unlike other optical detection methods used in biosensors (e.g. fluorescence), ECL is a highly sensitive and selective method because it does not require an exciting light source. Thanks to the numerical design of our planar micropore (20 µm x 10 µm), BPE wireless ECL was first obtained with deoxidization of the micropore [4]. Here we present wireless ECL obtained with a rhombus like gold deposit (6 µm x 3 µm) present at the bottom for the same oxidized planar micropore. For both cases, applied voltages (a few volts) were two orders of magnitude lower than standard BPE setups.

### Numerical Simulation

The dimensioning of the microdevice was carried out by numerical simulation using Comsol Multiphysics™. The complex AC Electrokinetic equation was solved on the 3D planar pore geometry.

Here we present our numerical results for designing Wireless Electrochemiluminescence Imaging microdevices based on a planar micropore restriction in which a BPE rhombus like (6 µm x 3 µm) gold layer was deposited (figure 1 right).

## Wireless ECL planar micropore device numerical model

### 3D geometries

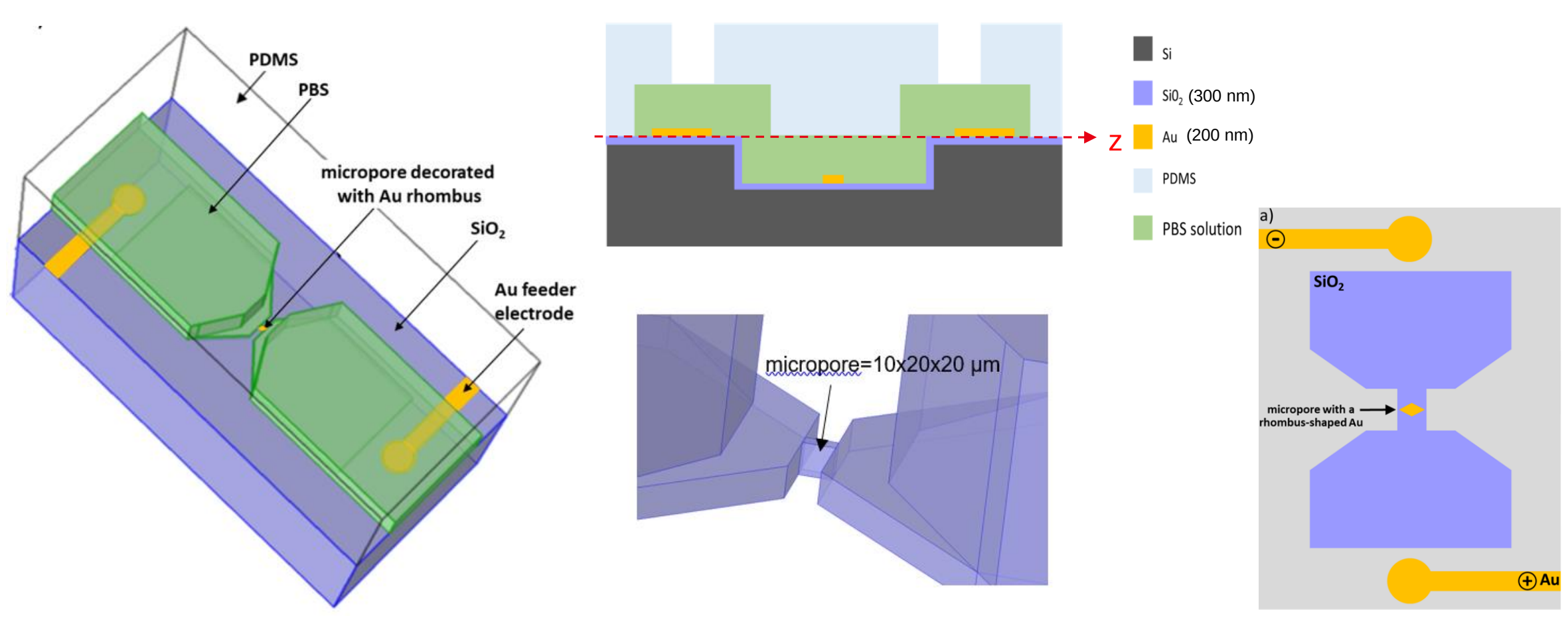
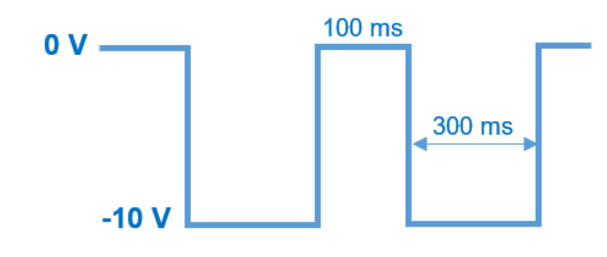


***Fig1: Geometrical description of the wireless ECL microchip. Left**: 3D view of the Si microchip covered with a PDMS mold (transparent color) that was specifically designed in order to fill the planar micropore with the solution composed of Phosphate Buffer Saline (PBS) and ECL reagents (green color). **Upper middle**: side view of the microchip (not to scale). **Lower middle**: zoom on the microdevice micropore. **Right**: microchip top views (not to scale): BPE obtained in the micropore with a rhombus like gold deposit (6 µm x 3 µm) (yellow).*

### Electrical parameters



*Example of voltage pulses applied for wireless ECL.*

| | σ [S/m] | $\varepsilon_r$ |
|---|---|---|
| Si | $7.1\ 10^6$ | 11 |
| SiO2 | $10^{-14}$ | 4.5 |
| PBS | 1.39 | 78.5 |
| Au | $45\ 10^6$ | 1 |

*Electrical parameters values.*

### Mathematical model

As voltage pulses are applied to the Au electrodes, the AC electrokinetic equation, deduced from Maxwell theory, is solved using the Finite Element Method implemented in Comsol Multiphysics™ :

$$\vec{\nabla}.\left(-(\sigma+i\omega\varepsilon)\vec{\nabla}V^*\right)=0$$

where σ is the electrical conductivity (S/m) of constitutive materials and fluids, ε their dielectric permittivity and ω the applied angular frequency (rad/s) of the applied voltage. V* is the complex electrical potential whose real part is the electrical potential acting on the ECL reaction:

$$\mathrm{V}=\mathrm{Re}(V^*),\vec{\mathrm{E}}=-\vec{\nabla}V$$

At the electrode surfaces where a voltage of 10V of frequency f is applied: $V_{electrode+}=+5V$

$$V_{electrode-}=-5V$$

Boundary conditions consider insulated all other microdevice boundaries :

$$-\vec{\nabla}V.\vec{n}=0$$

Thanks to its insulating character and its very low thickness, the $SiO_2$ layer (300 nm) is modelized using the contact pairs Comsol function.

As the objective of this numerical model is to quantify the influence of the geometrical restriction formed by the micropore on the electric field, the Electrical Double Layer formed at the gold electrode surface in contact with the saline solution, is neglected [5].

## Results & perspectives

### Numerical study of the planar micropore device

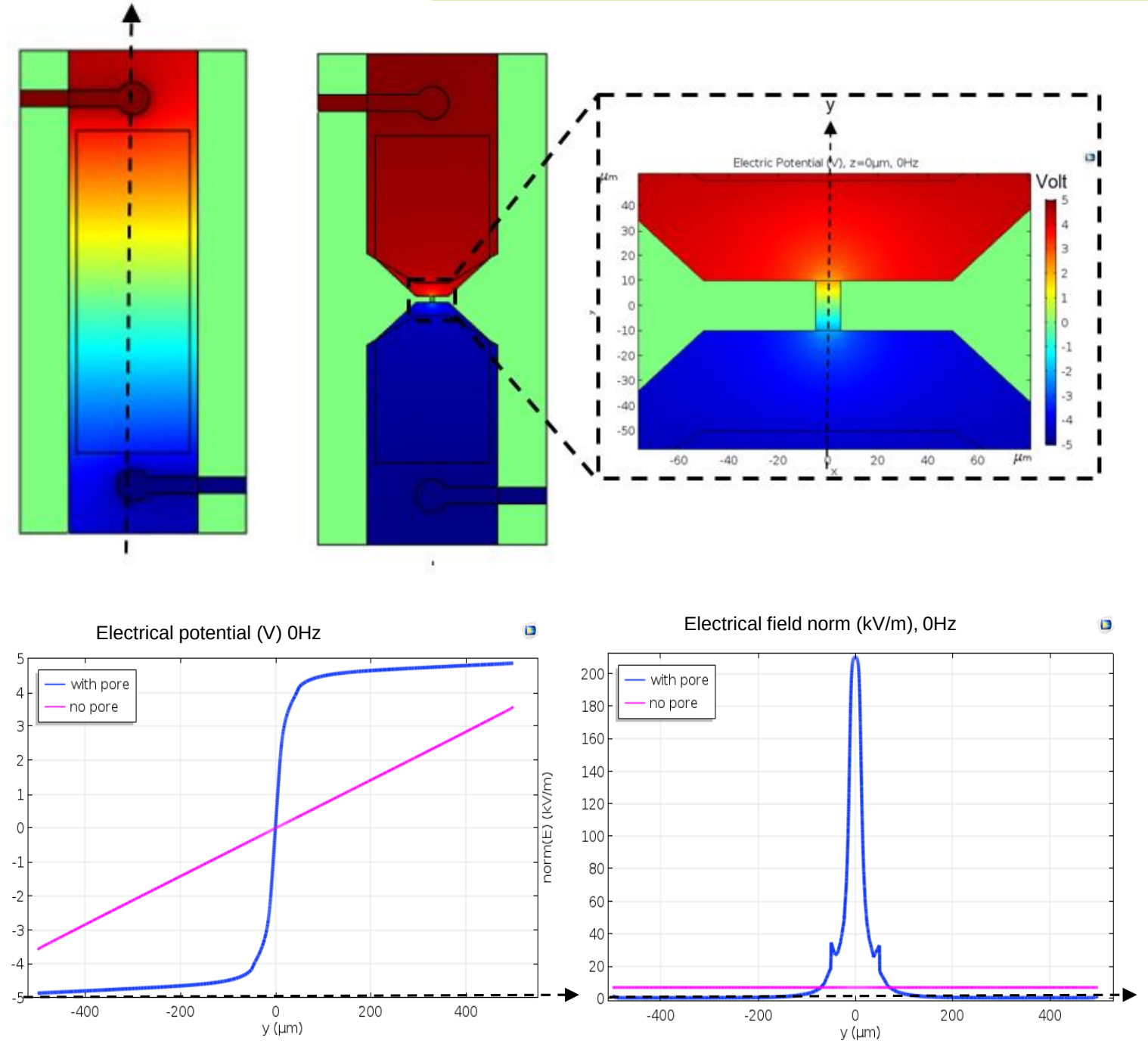


***Fig. 2: Comparison of the microchip without micropore (upper left, lower pink lines and the microchip with micropore (upper right, lower blue lines):** The ECL reaction is possible thanks to the micropore restriction which concentrates all the potential drop (upper right and lower left blue line) and the much higher magnitude of the corresponding electric field (lower right blue line). BPE is not present in the micropore for this computation.*

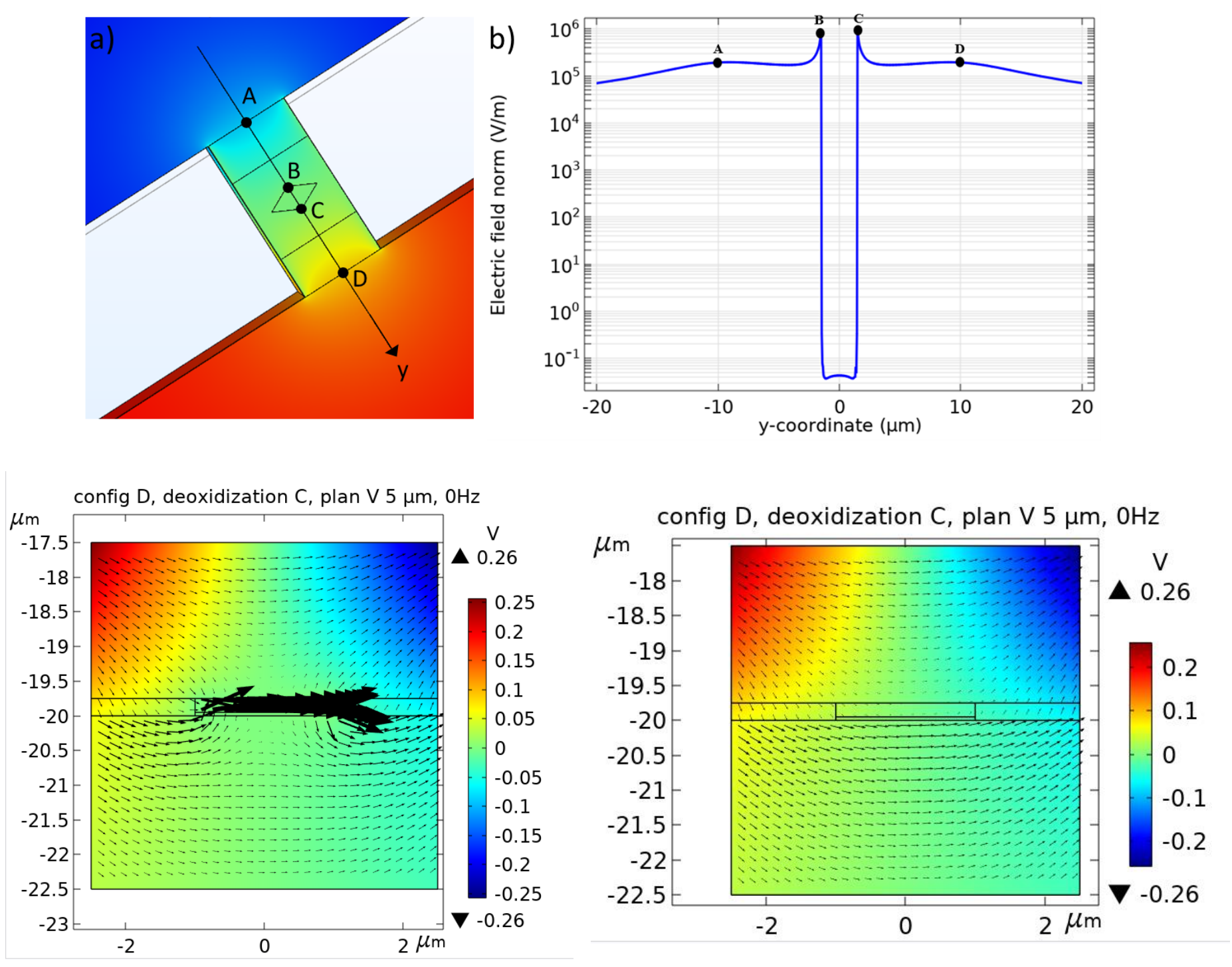


***Fig. 3: BPE rhombus like gold layer inside the micropore**: Potential distribution in the micropore (upper left), corresponding electric field norm along the micropore (upper right).*
*Side view of the potential and current density distributions in the vicinity of the BPE (lower left), comparison with the micropore without BPE (lower right).*

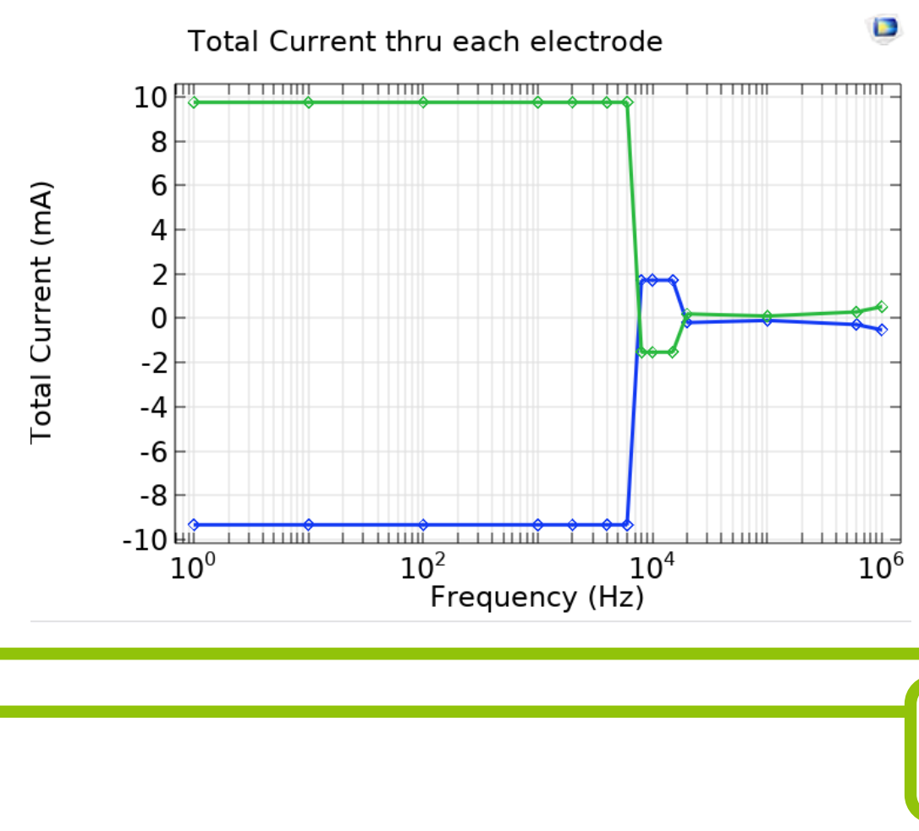


***Fig. 4: Computed total current at each feeder Au electrode vs. Frequency:** the total current conservation validates the numerical model (mesh size). This plot also shows that, above 8 kHz, the total current is varying as a consequence of the dielectric nature, dimensions and layout of the constitutive microchip materials.*

### Wireless ECL detection in the micropore with the rhombus like Au deposit

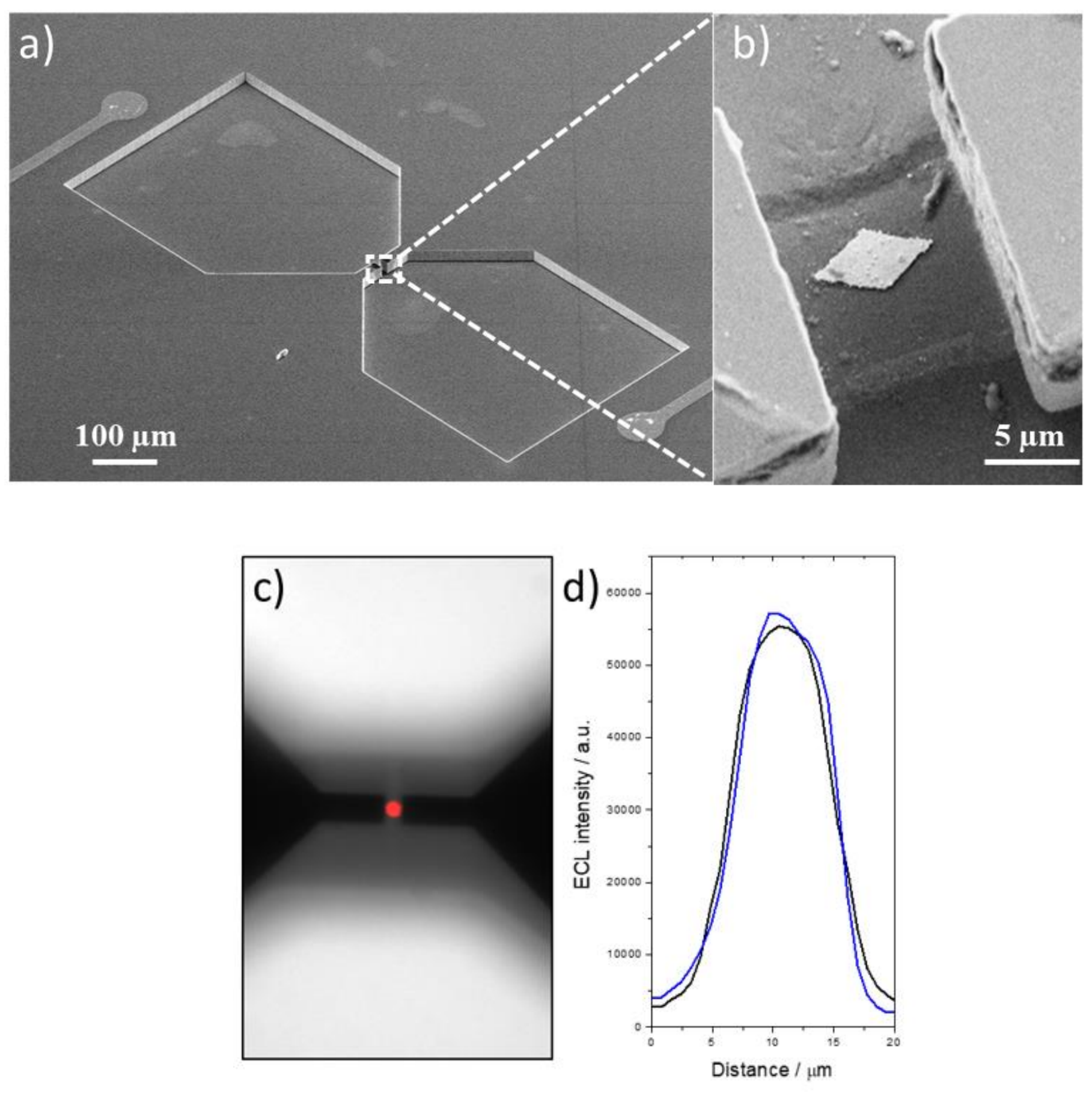


***Fig 5: Wireless ECL obtained with a BPE rhombus like gold layer inside the micropore: a)** SEM image of the microchip with the micropore (10 µm x 10 µm x 20 µm) and the integrated feeder Au electrodes. **b)** Zoom on the ECL-emitting rhombus-shaped Au layer (6 µm x 3 µm) (BPE) positioned at the bottom surface of the micropore. **c)** ECL-emitting BPE confined in the micropore. The ECL image was recorded in PBS (pH 7.4) containing 1 mM $[Ru(bpy)_3]^{2+}$ and 50 mM TPA by applying a sequence of 10 potential pulses of 10 V for 0.3 s followed by 0 V for 0.1 s, respectively. **d)** ECL intensity profiles along both normal axes along the short (blue curve) and the long (black curve) diagonals of the rhombus.*

### Conclusion & perspectives

Numerical simulation is a tool for *in silico* experimentation that allows the design of micro-devices for which macroscopic dimensioning rules are no longer relevant. Here we show numerically and experimentally that a possible application of micro-BPE is wireless ECL.

Prior to wireless ECL experiments, several numerical model parameters (solution conductivity, micropore size) have been varied in order to quantify their influence on the electric field level inside the micropore (not shown).

The numerical tool should be validated by electrical characterization (Electrical Impedance Spectroscopy).

Future work could concern the development of a more complete numerical model that could be developed to better represent electrochemical microsystems: the coupling of electrical quantities with the transport equations of electrochemical species and their reaction on the microBPE, taking into account the Electrical Double Layer on the metallic surfaces, etc...

This numerical tool should lead to the design of electrochemical microsystems not envisaged to date.

### References

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