Accurate and Simplified Consideration of the Probe Geometrical Defaults in SECM: Theoretical and Experimental Investigations

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Supporting Information

I.1. Simulation.

A commercially available program, Comsol®,[19] which allows numerical resolution of differential equations based on finite elements, has been used for the resolution of the diffusion equation in the previously described geometries. The steady-state simulations have been performed in 2D (cylindrical geometry) for the ideal and recessed cases and in 3D for all the other cases. When possible, the special features of the geometry have been used to reduce the size of the simulated domain: in the situation of an elliptic conductive part, the geometry has two planes of symmetry, so that only a quarter of the total geometry has been considered. In a similar way, in the off-centered microdisk situation, as well as in the tilted one, the geometry has one plane of symmetry so that only half of the total geometry has been considered.

In order to obtain reliable numerical results, some specific points have focused our attention. First, the size of the simulation domain, that is to say the distance between the external frontiers (where a condition c = 1 is applied) and the electrode has been checked to be large enough to have negligible impact on the calculated current. For this, larger domains for large L values have been used. Secondly, the meshing has been the subject of a special attention. It has been performed step by step, in three subdomains that have been artificially introduced to ease the meshing procedure. In order to diminish the number of meshes and the calculation time, a larger growing factor of the mesh has been used far from the tip. It has been checked that the obtained mesh had a minor impact on the evaluated current. Finally, the tip current has not been directly evaluated from the calculated concentration field. It has to be evaluated through the use of a special function implemented in the software, named “reacf”,[19] that showed much better accuracy and a much lower mesh dependency.

In order to have acceptable computing times, 3D simulations are performed with a slightly lower accuracy than 2D results. To quantify the impact of this aspect, comparison between 3D calculations and 2D calculations have been performed in the cases where it was possible ($\alpha = 0$, $H = 0$, $Off = 0$, and $b/a = 1$). As an example, the difference between the current obtained by the 2D and 3D simulations (obtained for $Off = 0$ and $R_g = 10$) are smaller than 0.005. This difference is considered as acceptable in regard to the following results and discussions.

I.2. fitting procedure for the determination of the apparent geometry.

Once theoretical negative and positive feedback approach curves are obtained for a given tip geometry, the apparent microdisk geometric parameters are determined using simultaneously the positive and the negative feedback approach curves. The fitting procedure uses nonlinear fitting algorithm available, for example, in the Nonlinear fit toolbox of Mathematica®.[20] Firstly, for fitting procedure, data of microdisk with perfect geometry are used. Positive and negative feedback currents for different R_g microdsik are therefore obtained from numerical simulations and constitutes about 2000 triplets $\{L, R_g, \psi\}$, with L between 0.03 and 30 and R_g between 1.01 and 100. Using the interpolation tool of Mathematica®, two continuous functions for dimensionless negative and positive feedback currents, $\psi_{neg}(L, R_g)$ and $\psi_{pos}(L, R_g)$, are generated.

In the second step, the fit is simultaneously performed on positive and negative feedback approach curves, with the same reference position (same $L_{0,app}$). This requires the adjustment of the parameters with 2 fit functions (Ψ_{neg} and Ψ_{pos} introduced just below), that is, to the best of our knowledge, not implemented in the Matlab version we have used. The following function has thus been used:

$$F(d,a,R_g,L_{0,app}) = \frac{|d|-d}{2|d|}\times a\times \psi_{neg}(-\frac{d}{a}+L_{0,app},R_g) \quad + \quad \frac{|d|+d}{2|d|}\times a\times \psi_{pos}(\frac{d}{a}+L_{0,app},R_g)$$

This function is equal to Ψ_{neg} for negative values of the first parameter *d,* and Ψ_{pos} for positive values. It is the 3 last parameters of this function (a, R_g and $L_{0,app}$) that have been adjusted to fit to several experimental or calculated data sets. The latter were constructed by merging the negative feedback data to the positive feedback data, after multiplication of the negative feedback distances by –1.

I.3. Apparent parameters and estimated error

I.3.1. Tip-to-substrate misalignment. The theoretical study is done for a microdisk with $R_g = 2$ and different approaches with tilt angles between 0 and 10°. Figure SI1 shows the apparent zero distance values $L_{0,app}$ of the best perfect disk-like behavior for tilt angles between 0 and 10°. See discussions in the main text.

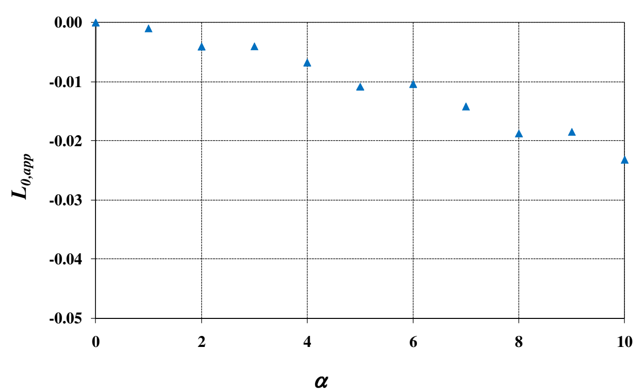


Figure SI1. Zero tip-substrate distance, $L_{0,app}$, of the disk-like behaviour of different tilted microdisk $R_g = 2$ tips (▲).

I.3.2. Recessed electrode. In order to have a closer look at this situation, several positive and negative feedback curves for different R_g and H have been calculated, and then fitted with a perfect (non recessed) microdisk. Figure SI2 gathers for different microdisks (R_g = 2 and R_g = 10) with different recesses (H between 0 and 1.5), the three geometric parameters (a_{app}, $R_{g,app}$, $L_{0,app}$) of the best perfect disk-like behavior and the corresponding error. See discussions in the main text.

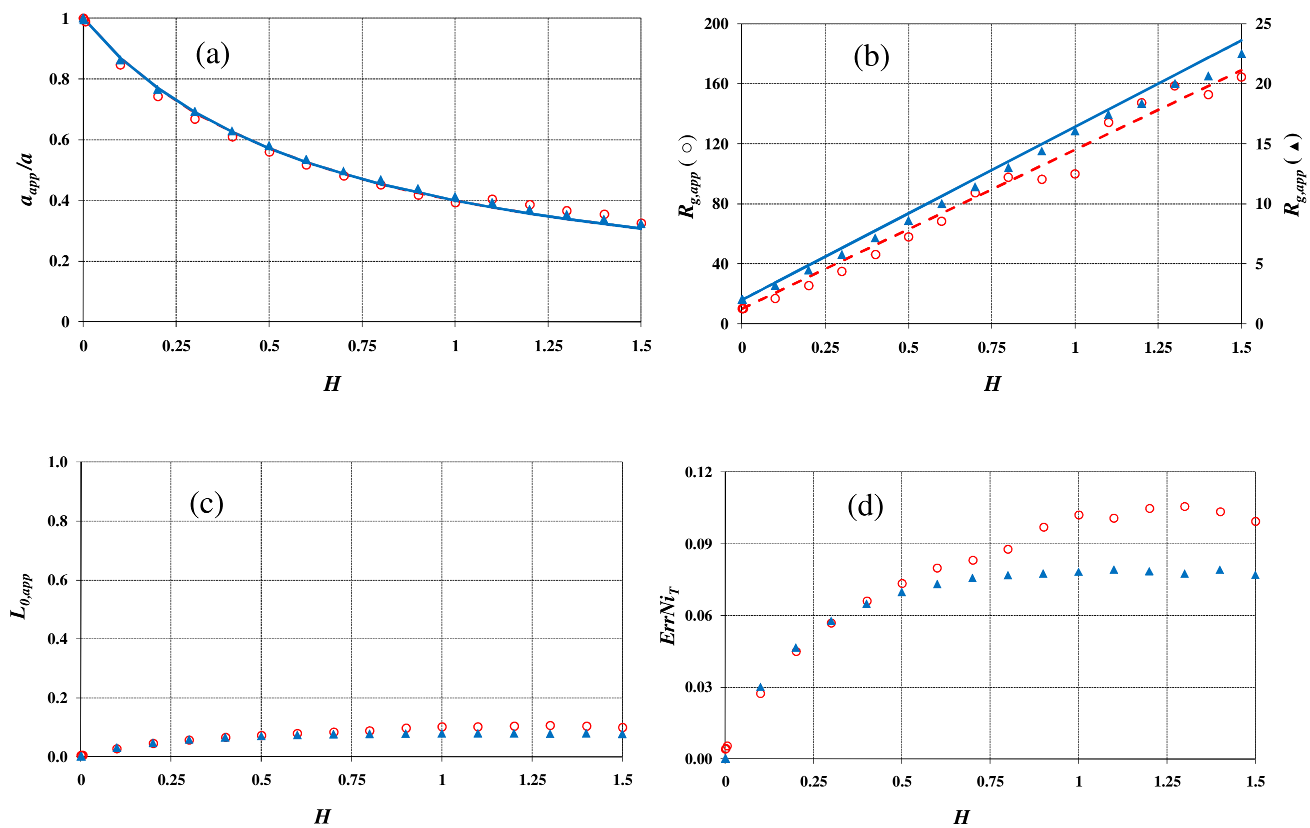


Figure SI2. Geometric parameters of the disk-like behaviour of different recessed microdisk tips. (a): disk radius a_{app}/a as a function of the recess depth H. (b): insulator radius, $R_{g,app}$ as a function of H. (c): zero tip-substrate distance, $L_{0,app}$ as a function of H. (d): maximal error on the current. The following symbols are used: ○ for R_g = 10 and ▲ for R_g = 2. Lines show analytical approximations for a_{app} and $R_{g,app}$. (a): Eq.(5a), (b): Eq.(5b), continuous blue line for R_g = 2 and dashed red line for R_g = 10.

I.3.3 Microdisk with an offset of the conductive part. Figure SI3 shows the $R_{g,app}$, for a glass microdisk having an outer radius of 10 (or 2) and different *Off* values going from 0 to 9 (or from 0 to 1 for an outer radius of 2). The approximate expression (Eq. 6b) for $R_{g,app}$ is also shown on this Figure. See discussions in the main text.

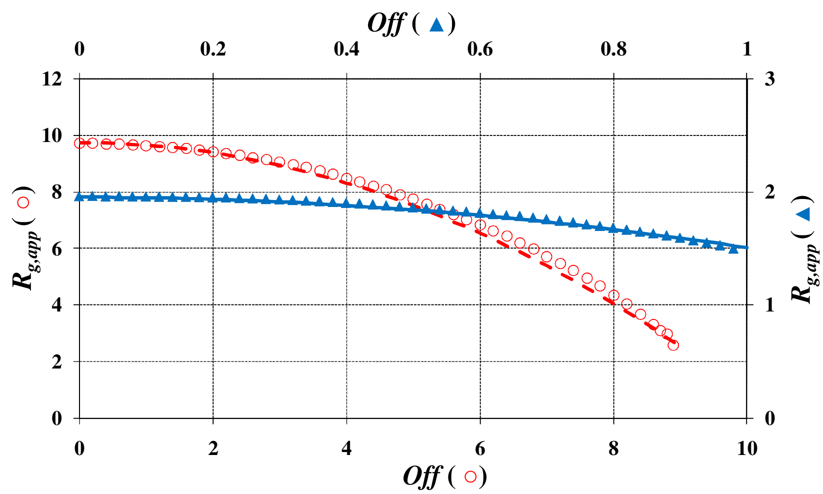
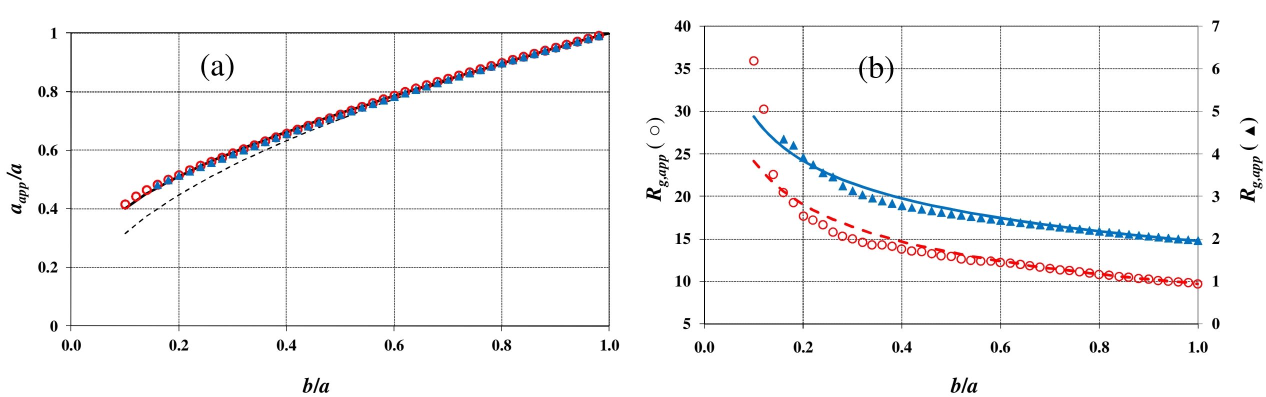


Figure SI3. Apparent R_g for different off-centered microdisk tips. The following symbols are used: ○ for $R_g = 10$ and ▲ for $R_g = 2$. Lines show analytical approximations for a_{app} and $R_{g,app}$. (a): Eq.(10a). (b): Eq.(10b), continuous blue line for $R_g = 2$ and dashed red line for $R_g = 10$.

I.3.4. Microdisk with an elliptic conductive part. Figure SI4 shows the three apparent geometric parameters (a_{app}, $R_{g,app}$, $L_{0,app}$) for a glass microdisk of $2\times R_g$ dimensionless diameter with $R_g = 10$ or $R_g = 2$ and different *b*/*a* ratio between 0 and 1. In Figure SI4a (apparent active radius) and SI4b (apparent R_g), the analytical approximations are also presented. See discussions in the main text.



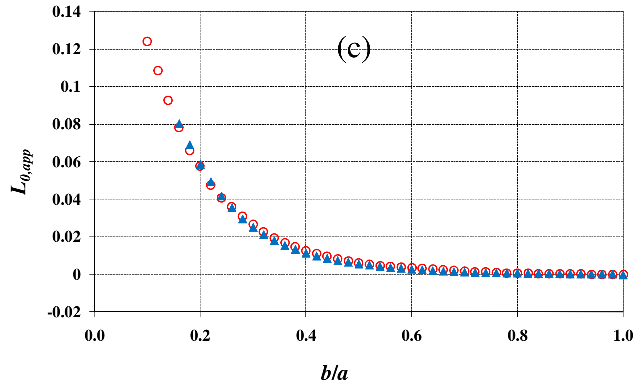


Figure SI4. Geometric parameters of the disk-like behaviour of different elliptical tips as a function of b/a (a): disk radius a_{app}/a (b): insulator radius, $R_{g,app}$ (c): zero tip-substrate distance, $L_{0,app}$. The following symbols are used: ○ for $R_g = 10$ and ▲ for $R_g = 2$. Lines show analytical approximations for a_{app} and $R_{g,app}$. (a): dashed line $a_{app} = \sqrt{ab}$ and continuous line Eq. (7a). (b): Eq. (7b), continuous blue line for $R_g = 2$ and dashed red line for $R_g = 10$.

As shown figure SI4b, the analytical approximation for the apparent R_g does not exactly match the data for small b/a values ($b/a < 0.4$). However the slight difference between the values issued of the best fit or coming from the approximate expression does not lead to a big additional error. This comes from the relatively small influence of R_g on the current. For example, for $R_g = 10$ and $b/a = 0.3$, the fit gives $a_{app} = 0.59\times a$ and $R_{g,app} = 15.0$ with an error of 1.8 % while the approximate expressions give $a_{app} = 0.59\times a$ and $R_{g,app} = 16.4$ with a hardly larger error of 2.0 %.