Microfluidic Push-Pull Probe for SECM

--Electronic Supporting Information--

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SI-1. Finite element simulations of SECM approach curves with soft probes

The computational model assumes the probe (parallelepiped with dimensions 125 μm · 1000 μm · 1000 μm) in a box-shaped domain (3000 μm · 2000 μm · {1000–2000} μm) that represents a solution bulk (see Figure S-1). The active area of the microelectrode was approximated to a quarter-moon shape (*i.e.* 20 μm depth and 40 μm width). The probe was approached to the substrate at an inclination angle (〈) equal to 70 degrees. The approach curves started at a probe-substrate distance of h_P = 1000 μm and 20 further points were calculated until touching the substrate. After the probe touched the substrate, the probe bending was assumed by changing the inclination angle 〈 for 4 to 6 new probe positions.

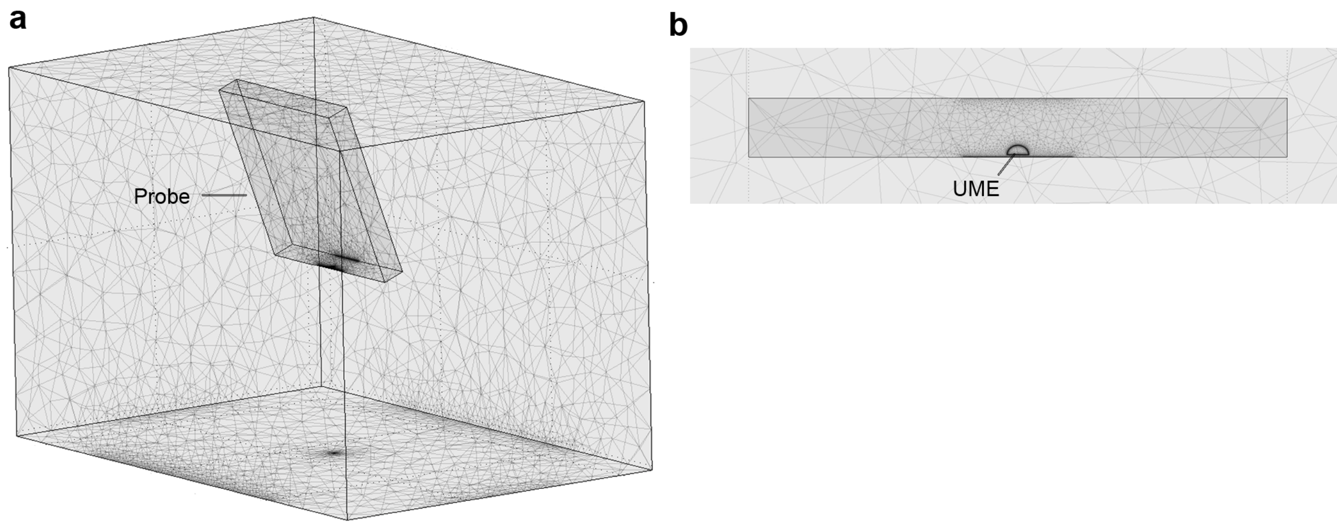

Figure S-1. A general representation of a computational domain with mesh (a) and magnification of an exposed tip area (b).

Typical mesh consisted of 22000 – 62000 mesh points that is approximately equal to 120000 – 360000 tetrahedral mesh elements. Consequently, the model was solved in a dimensional form for up to 365000 degrees of freedom assuming steady-state diffusion of electroactive species:

$$\nabla(-D_i \nabla c_i) = 0 \qquad \text{(SI–1)}$$

where D_i and c_i are the diffusion coefficient and concentration of species i, respectively. We assume the electrochemical reaction of redox mediator O which takes place at the tip

$$O - e^- \xrightarrow{k_1} R \qquad \text{(SI–2)}$$

and its recycling at the substrate

$$R + e^- \xrightarrow{k_2} O \qquad \text{(SI–3)}$$

Consequently, reaction rates at the tip (v_{tip}) and substrate (v_{sub}) are considered as

$$v_{tip} = k_1 * c_o \quad \text{(SI–5)}$$

$$v_{sub} = k_2 * (c_{bulk} - c_o) \quad \text{(SI–6)}$$

with rate constants k_1 and k_2, respectively, and assuming initial bulk concentration of the redox mediator c_o = 2 mM. In the present study we assume steady-state diffusion limited conditions, *i.e.* $k_1 = k_2 = 10^6$, and the equality of diffusion coefficients for both species *O* and *R*, *i.e.* $D_O = D_R = 6.7 \cdot 10^{-10}$ m^2 s^{-1}, which corresponds to diffusion coefficient of ferrocene methanol in water.

The boundary conditions employed in the FEM simulations are collected in the Table S-1 (**n** indicates vector normal to the surface)

Table S-1. Boundary conditions for FEM simulations.

Surface	**Boundary condition**
Active surface of electrodes	Flux, $\mathbf{n} \cdot D\nabla c_o = -k_1\, c_o$
Body of electrode	Insulation, $-\mathbf{n} \cdot D\nabla c_o = 0$
Box planes: top and sides	Concentration, $c_o = c_{bulk}$
Box planes: bottom	Insulation, $-\mathbf{n} \cdot D\nabla c_o = 0$ or Flux, $\mathbf{n} \cdot D\nabla c_o = -k_1\,(c_{bulk} - c_o)$

Numerical solution of the system of differential equations was made using a linear system solver (conjugate gradients) with an algebraic grid preconditioner and a relative error tolerance of $1 \cdot 10^{-6}$.

The new vertical coordinate h_P in contactless mode was described as the distance between the substrate and the lowest point of the soft probe (see Figure S-2). Consequently, h_P approaches zero when the probe gets into a contact with the sample. The further pressing the probe against the substrate would consequently result in negative h_P values. The computations were carried out assuming probe bending as changing probe inclination angle, so the h_P in a contact mode was calculated as

$$h_P = l_P(\sin\alpha - \sin\gamma) \quad \text{(SI–7)}$$

where γ represents the inclination angle due to the probe bending and l_P corresponds to the probe length.

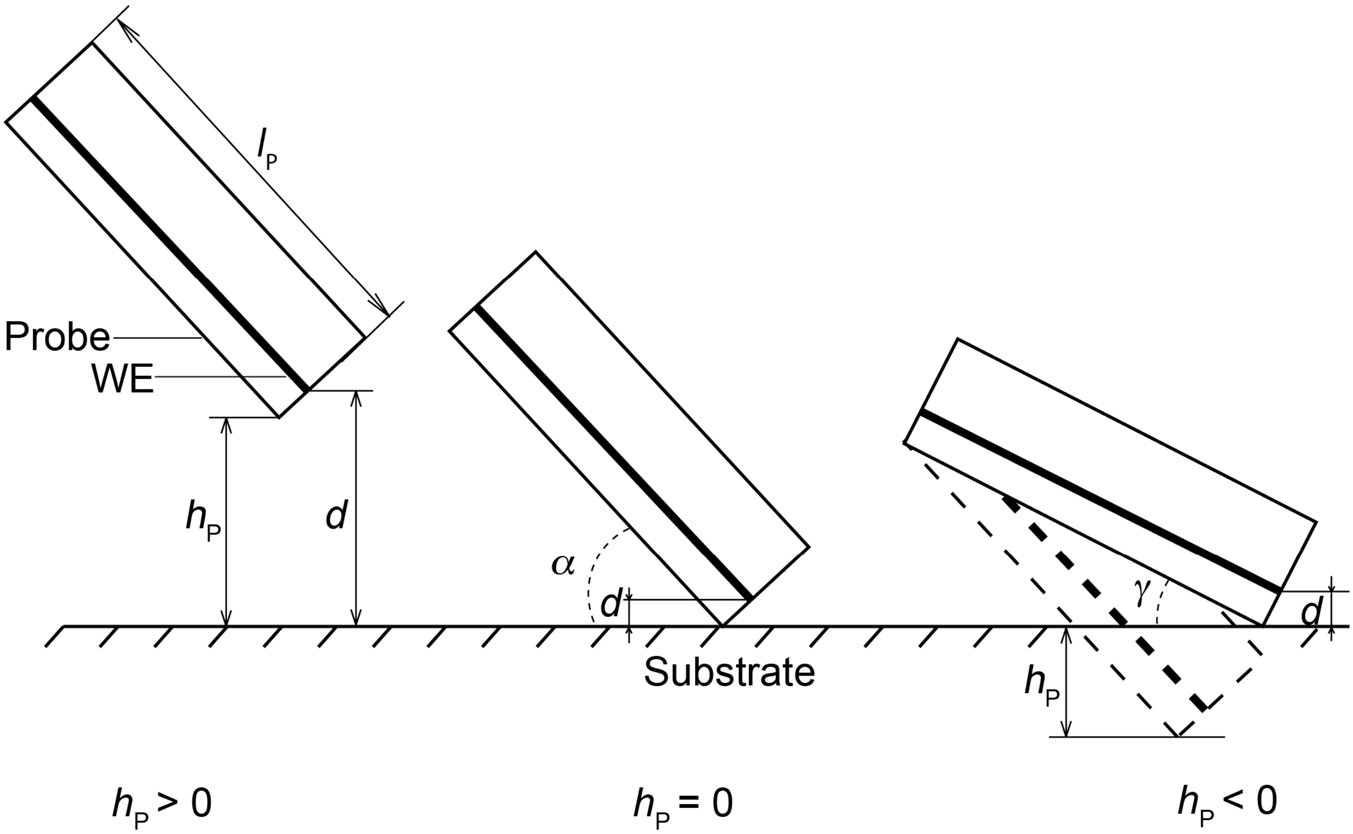

Figure S-2. The illustration for contact and contactless SECM mode for soft probes. The vertical coordinate, probe-substrate distance, probe length, probe inclination angles in contact and contactless mode are represented as h_P, d, l_P, α and γ respectively.

SI-2. Droplet size estimation

When the probe is in a contact with a substrate the electrolyte droplet can be assumed as a prism with triangular cross-section (see Figure S-3). The probe thickness (125 μm), the probe inclination angle and the probe width (~3 mm) define the geometrical parameters of the droplet. Thus, the volume can be calculated as:

$$V = \frac{1}{2} * 125 * 10^{-6} * \cos\alpha * 125 * 10^{-6} * \sin\alpha * 3000 * 10^{-6} = 7.53 * 10^{-12} m^3$$

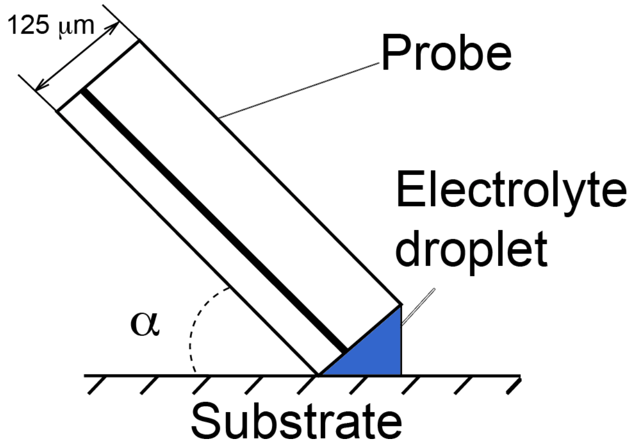

Figure S-3. The scheme for estimation of droplet size. The triangular cross-section of the electrolyte droplet is marked with blue and the probe inclination angle is specified as α.

SI-3. Calculations of a minimal working distances for soft probes in contact mode

Figure S-4 demonstrates the dependence of a of minimal probe-substrate distance *d* on probe inclination angle α and angle of exposure β. For the case described in the present paper (*i.e.* α = 70°) we can assume linearity, as shown on Figure S-5.

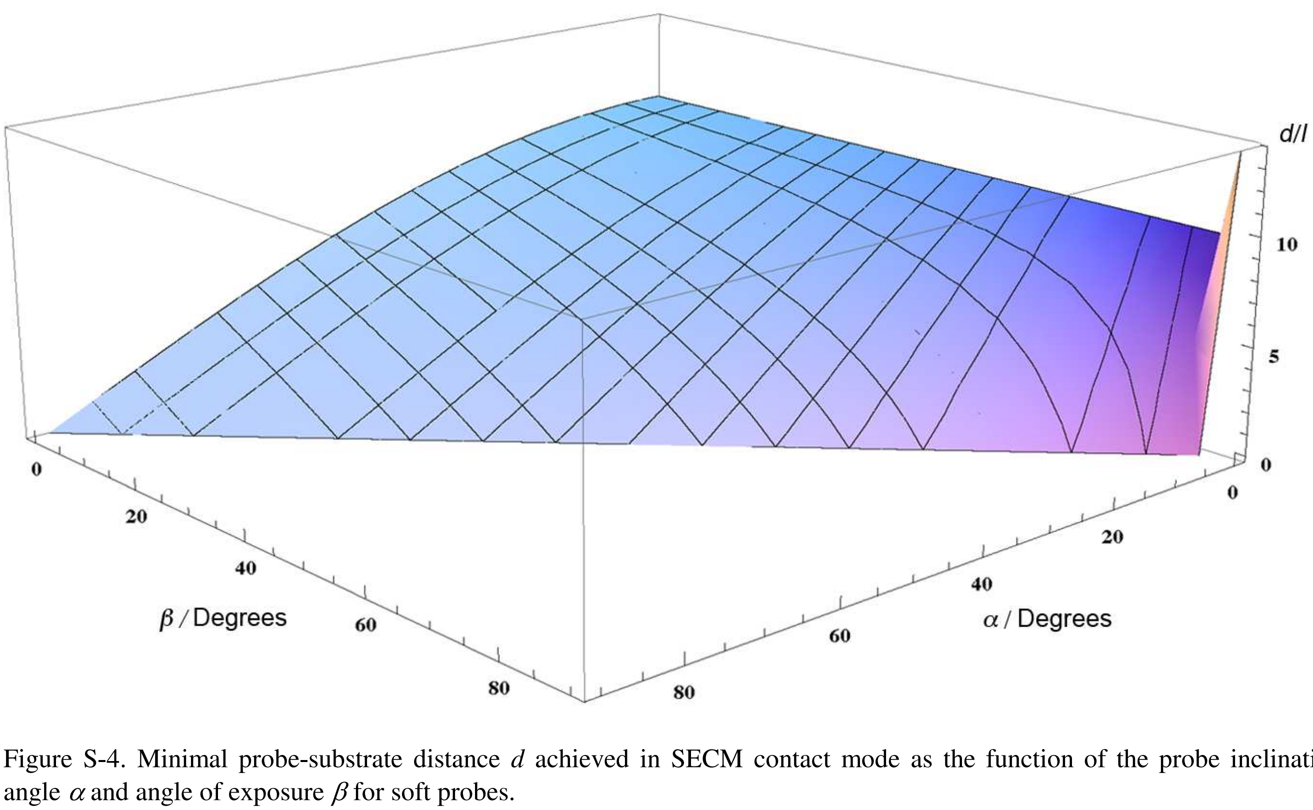

Figure S-4. Minimal probe-substrate distance *d* achieved in SECM contact mode as the function of the probe inclination angle α and angle of exposure β for soft probes.

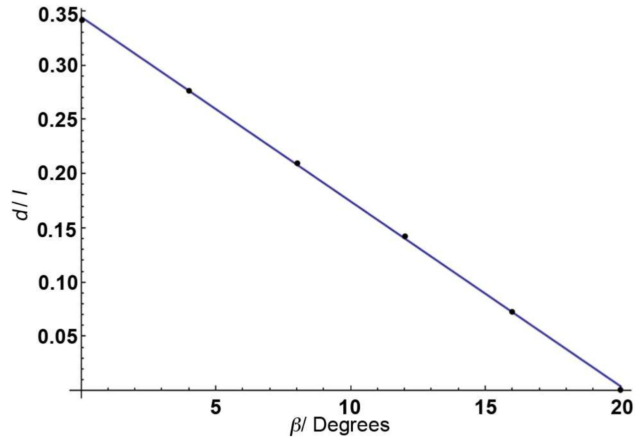

Figure S-5. Calculated minimal probe-substrate distance d achieved in SECM contact mode as the function of the angle of exposure β in assumption of probe inclination angle $\alpha = 70º$. Solid line represents linear approximation of the exact solution (dots).

SI-4. Nanodroplet stability at the tip of the probe

The issue of the nanodroplet stability is very important when discussing SECM experiments on initially dry samples. The provided video files reveal how the droplet is held between the probe and the substrate and how the droplet size changes due to the unbalanced microfluidic flow rates. Figure S-6 depict the setup employed for recording these video files.

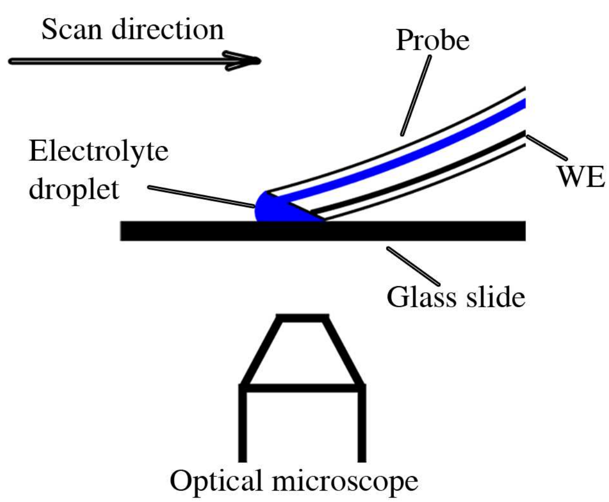

Figure S-6. Schematic representation of the setup for investigation of a scanning process in a contact mode.